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University of Alberta

PHASE BEHAVIOUR FOR THE SYSTEM HYDROGEN SULFIDE-CARBON DIOXIDE- METHANE

by

JOHN ALAN BAILEY

February 1, 1957

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PHASE BEHAVIOUR FOR THE SYSTEM $H_2S-CO_2-CH_4$

A DISSERTATION
SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

FACULTY OF ENGINEERING
DEPARTMENT OF CHEMICAL
AND
PETROLEUM ENGINEERING

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ABSTRACT

The isothermal phase behaviour of the three component system: hydrogen sulfide, carbon dioxide, and methane was studied at a temperature of 100 degrees F. The experimental procedure entailed the preparation of mixtures in the gas phase which were then compressed into the two phase liquid-vapor region. Three series of tests were conducted at pressures of 600, 1200 and 1800 lb/in.^{2}abs. The compositions of the resulting co-existing phases at the particular pressure were analytically determined. The data obtained specified the locus of the liquid-vapor phase boundaries within the two phase region existing from 410 lb/in.^{2}abs. to 1910 lb/in.^{2}abs.

Equilibrium constants calculated for each component at the pressures studied permitted the prediction of phase compositions at the intermediate pressures of 900 and 1500 lb/in.^{2}abs. The nature of the system deviations from idealized liquid-gas behaviour were expressed by calculation of activity coefficients. Compressibility factors were obtained from experimental observations on the gas phase. The experimental results indicated that at low pressures the actual phase compositions approximated the values predicted by the ideal solution law. However, at 1200 lb/in.^{2}abs. and at higher pressures, considerable deviation occurred. At pressures above 1075 lb/in^{2}abs. the system forms a locus of ternary critical points. Over this pressure range the compressibility factors and activity coefficients were functions of system composition and pressure. However, at pressures below the critical point formation the deviation of the system from ideality was primarily a function of pressure.

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LIST OF SYMBOLS AND DEFINITIONS

c -The components in a system

C -Composition parameter equal to the ratio of mole fractions of carbon dioxide in the vapor phase to the carbon dioxide in the vapor phase plus the methane in the vapor phase.

F -Number of variables or degrees of freedom in a system.

F. -Units of temperature in Fahrenheit degrees.

ϕ -The phases in a system.

γ -Activity Coefficient.

K -Equilibrium constant .

n -Moles in the gas phase.

lb/in.^{2}abs -Units of absolute pressure in pounds per square inch.

p -Partial pressure in gas phase.

P^* -Vapor pressure.

π, P -Absolute system pressure.

R -Universal Gas constant.

T -Absolute temperature of the system in degrees Rankine.

V -Volume of the gas phase.

X -Mole fraction of the component in the liquid phase.

Y -Mole fraction of the component in the vapor phase.

Z -Compressibility Factor and

Z_m -Mean compressibility Factor .

SUBSCRIPTS

A -Referring to Component A.

B -Referring to Component B.

i -Referring to any Component i.

1 -Referring to carbon dioxide.

2 -Referring to hydrogen sulfide.

3 -Referring to methane.

I INTRODUCTION

The compositions of liquid and gas phases in equilibrium is of considerable importance in many industrial processes. These operations depend on the determination of the component concentration gradients existing between phases. Considerable experimental data for this purpose is available on the low vapor pressure, high boiling point systems. Nevertheless, there is a dearth of published information for the low boiling point components which normally exist in the gaseous state. While attention has been focussed on gaseous hydrocarbons for the refining industries many non-hydrocarbon systems have been neglected, particularly for three or more components.

The lack of data is primarily due to the difficulty in the construction and operation of equipment which is sufficiently adequate to yield quantitative phase data. Although equations are available to predict the compositions of phases existing at equilibrium, they are limited in scope by assumptions employed in their deviation. Experimental data are also required to determine constants in the equations for a particular system. Therefore, although an extensive experimental program for a given system is time-consuming, it is the best means now available for the determination of phase equilibrium.

This report describes the design and operation of experimental equipment used to determine liquid-vapor phase relations in the ternary system hydrogen sulfide, carbon dioxide, and methane at pressures up to 1800 lb/in.^{2}abs. This particular system was selected since no prior published data seemed to be available even though the system was of some commercial importance. The existence of information on the binary pairs facilitated

the investigation on the three component system by predicting the pressure and composition ranges over which the ternary systems would form two phases.

II BACKGROUND OF PHASE BEHAVIOUR

The theoretical development of liquid-vapor phase behaviour was initiated by the postulation of basic laws related to the nature of the gaseous state.

Robert Boyle in 1662, Charles in 1787, and Gay Lussac in 1802 carried out the first experiments on the behaviour of gases. The combined gas law resulted from their work. It correlates the pressure, volume and temperature behaviour of ideal gases.

Investigations into the relationships between the liquid and gaseous states commenced during the first of the nineteen century. In 1822 Caignard de la Tour (7), in a series of historical experiments determined the existence of critical states in the alcohol-water-ether system. By 1823 the first "fixed" gases of the low boiling point liquids chlorine, hydrogen sulfide, carbon dioxide and ammonia had been liquified by Michael Faraday and Sir Humphrey Davy (7).

Previous to this time, these gases had been considered non-condensable. By 1845 Faraday had determined the vapor pressures of 11 pure components, as well as the critical temperature and pressure of carbon dioxide. (7).

The first investigator to obtain complete phase behaviour data for a pure component in the liquid and vapor regions was Andrews in 1869. He determined the behaviour of carbon dioxide and discussed the continuity of liquid and gas states near the critical temperature.

Laws developed during this period for two phase equilibrium included Raoult's Law, Dalton's Law, and the fundamental Phase Rule of Williard Gibbs. Gibbs in 1876 related all types of heterogeneous equilibrium by correlating the possible degrees of freedom

to the number of components present and the number of phases existing in equilibrium.

The experimental work on systems of more than one component commenced in 1887 with Andrews who did work on the system carbon dioxide-nitrogen. During this interval which extended to the first part of the Twentieth Century various binary mixtures were studied primarily to determine the property changes which occurred in a pure component as a second was added to it.

Theoretical equations based on thermodynamic concepts of equilibrium were derived to predict phase equilibrium. These include the Margules and the Van Laar Equations.

By 1910 the theoretical aspects of vapor-liquid equilibrium were adequately covered and further experimental work was neglected. However, the need for data on particular systems occasioned by growing petro-chemical industries led to a revival of interest starting about 1930. Since that time much information on the behaviour of simple and complex systems has been obtained by several workers in the field (1) (4) (12).

III THEORY

1. Heterogeneous Liquid-Vapor Phase Equilibria

The thermodynamic state of a multicomponent system is completely defined by the intensive variables: pressure, temperature, and phase composition. The relation between variables for a system constitute phase diagrams. These define the pressure and temperature limits in which two phase equilibria may exist for a particular system as well as the compositions of existing phases.

Since a phase diagram is limited to three space dimensions, only three of the total variable may be represented simultaneously. The additional variables must be held at a fixed value for a given diagram. The variables in a system of c components total c + 1 including temperature, pressure and c - 1 composition variables. Therefore, the phase diagram for a two component system may be completely represented with three space coordinates.

2. Nature of Two Component Phase Diagrams

The phase variables for a two component system are temperature, pressure and the composition of one component. The variable relationships are indicated by use of three rectangular coordinates with pressure as ordinate and temperature, composition axes as abscissae. The composition axis is generally in terms of mole fractions.

The nature of the phases existing within the three dimensional phase coordinates may be defined with reference to Gibb's Phase Rule ([illegible]).

$$\phi + F = c + 2 \quad --- (1)$$

For a two component system the phase rule reduces to:

$$F = 4 - \phi \quad --- (2)$$

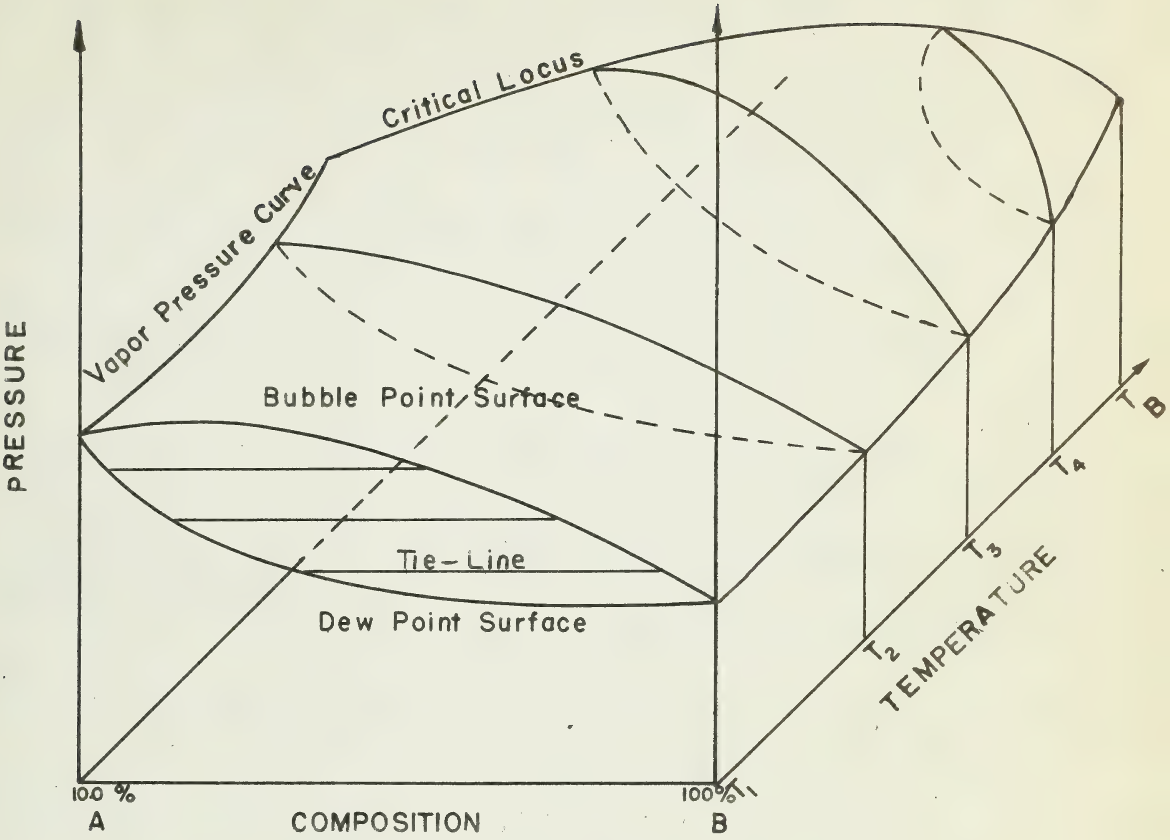


FIG. I.

TWO COMPONENT PHASE DIAGRAM

IN THE LIQUID VAPOR REGION

Homogeneous single state phases with a value of ϕ equal to unity will exist with three degrees of freedom according to the modified Phase Rule (2). Thus the liquid and vapor phases will be represented by three dimensional solid portions within the phase diagram.

System conditions permitting two phases to exist simultaneously in equilibrium cause a degree of freedom to be lost in the transition from a single phase. Only two of the three variables must then be specified to locate a given system. The locus of the boundaries between co-existing liquid and gas phases will then be a two dimensional surface, traced by a line to which one degree of freedom has been added. In general, the boundaries form two distinctly separate surfaces since both phases in equilibrium have different overall compositions. One surface indicates the compositions of the liquid or more dense phase existing within certain pressure limits and the other indicates the corresponding limits for the less dense phase.

The volume enclosed by the two surfaces is the heterogeneous two phase region. Any system at the temperature, pressure and composition conditions locating it within this region will separate into two co-existing phases.

Fig. 1 is the three dimensional representation of the phase diagram for a typical two component system A and B in the liquid-vapor range. Both components are mutually soluble in all proportions in the liquid state with no tendency to form azeotropes. The section comprises a temperature range from T_1 to a temperature past the critical temperatures T_A and T_B of both components.

The two pressure-temperature axes for the individual components

A and B indicate the vapor-pressure curves for the components. Both vapor pressure curves terminate at the critical temperatures T_A and T_B. In the diagram component B is represented as having a higher critical temperature than A and a lower vapor pressure at intermediate temperatures since it is the less volatile of the two.

The component is gaseous below the vapor pressure for a particular temperature and liquid above, the phase change occurring at the vapor pressure.

Whereas the transformation pressure from vapor to liquid is constant for the single component systems, intermediate two component systems at temperatures between T_1 and T_B will commence to liquify at the dew point pressure and become completely liquified at the higher bubble point pressure. The locus of the dew point pressures and compositions together with the corresponding bubble points form the two phase boundary surfaces enclosing the heterogeneous region.

The boundary surfaces intersect at the vapor pressure curves for the components at temperatures below the critical for both. However, between the critical points for A and B the two surfaces tend to merge and intersect at the two component critical locus. The two component critical locus represents the pressure and temperature conditions for the critical points of all the possible two component mixtures.

Typical isothermal pressure-composition sections through the heterogeneous region are indicated at the temperatures T_1, T_2, T_3 and T_4. The intersection of the sections with the heterogeneous region are shown by the dashed lines for the hidden dew point surface and the continuous lines for the upper bubble point surface.

The sections at T_1 and T_2 are below the critical temperature for A and consequently represent all intermediate mixtures between the vapor pressure curves of A and B. The isothermal sections at T_3 and T_4 typify sections at temperatures between the critical for both components. Both sections are terminated at the composition and pressure corresponding to the critical point for the temperatures T_3 and T_4.

The compositions of phases in equilibrium at different pressures in the heterogeneous region are represented by the isobaric tie-lines for the pressure composition section at T_1. Each isothermal section will have similar tie-lines.

3. Representation of Three Component Equilibria

While two component systems may be completely represented in three space coordinates, a three component system must necessarily have one of the variables restricted to a constant value for the same representation. The representation of the three dimensional phase diagram for three components can be indicated by holding the system temperature constant over the pressure range in which two phases exist. At the constant temperature the change of phase composition with pressure can be illustrated in three coordinates with pressure as the ordinate and two independent concentrations as abscissae. Temperature is generally selected as the invariant quantity since the usual design of equipment to determine phase equilibria favours maintenance of isothermal conditions during the test program.

The problem of representing the three dimensional system in two dimensions can be partially solved by the use of constant pressure sections taken through the complete isothermal phase diagram.

These isobaric sections representing the compositions of phases in equilibrium are plotted on equilateral triangular graphs. Use of triangular graphs permits the direct plotting of the two independent and the dependent concentration for a given point.

The complete phase diagram is thus represented within coordinates forming a right prism, each side representing the pressure-composition coordinates for a binary system. Any specific point within the prism represents a three component system and may be located by its pressure and the composition of two of the components.

4. Nature of Phase Diagrams for Three Components

The modified form of the Phase Rule (2) will again apply to illustrate the phase relationships since the increase in variance introduced by another component to the two component system, is balanced by the restriction of temperature to a constant value. Hence the nature of the various phase regions is analagous to those for the two component system.

The single state liquid and vapor phases existing with three degrees of freedom occupy solid portions of the phase diagram. Two dimensional surfaces again represent the phase boundaries between the homogeneous single phase regions and in general the surfaces are separate since contacting phases have a definite different composition fixed by the equilibrium state. Any system at conditions placing it within the heterogeneous region enclosed by the phase boundaries will separate into two simultaneously existing phases. The compositions of the two phases are indicated by the tie-lines at the temperature and pressure of the equilibrium intersecting the phase boundaries.

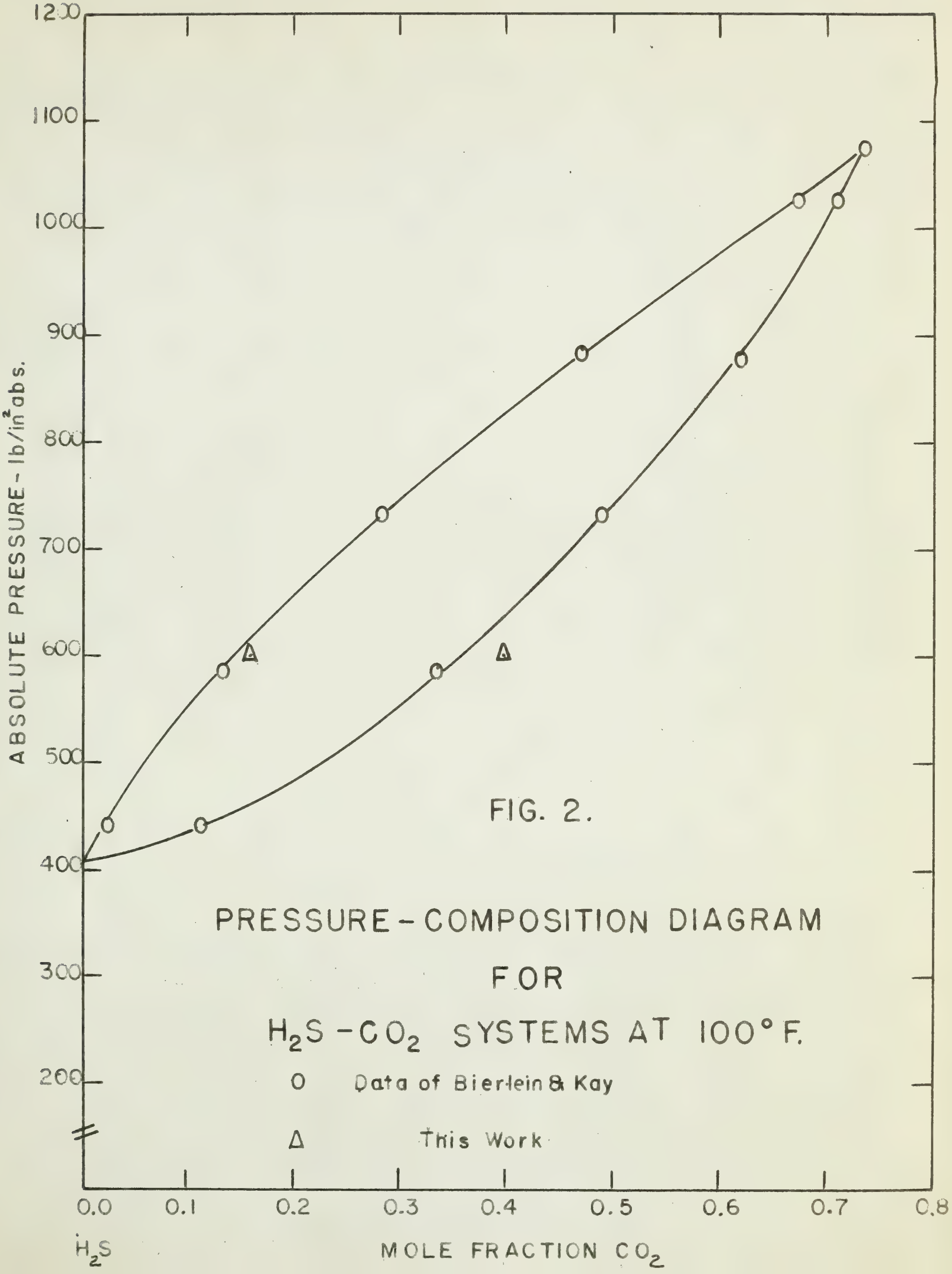


FIG. 2.

PRESSURE-COMPOSITION DIAGRAM FOR H_2S-CO_2 SYSTEMS AT 100° F.

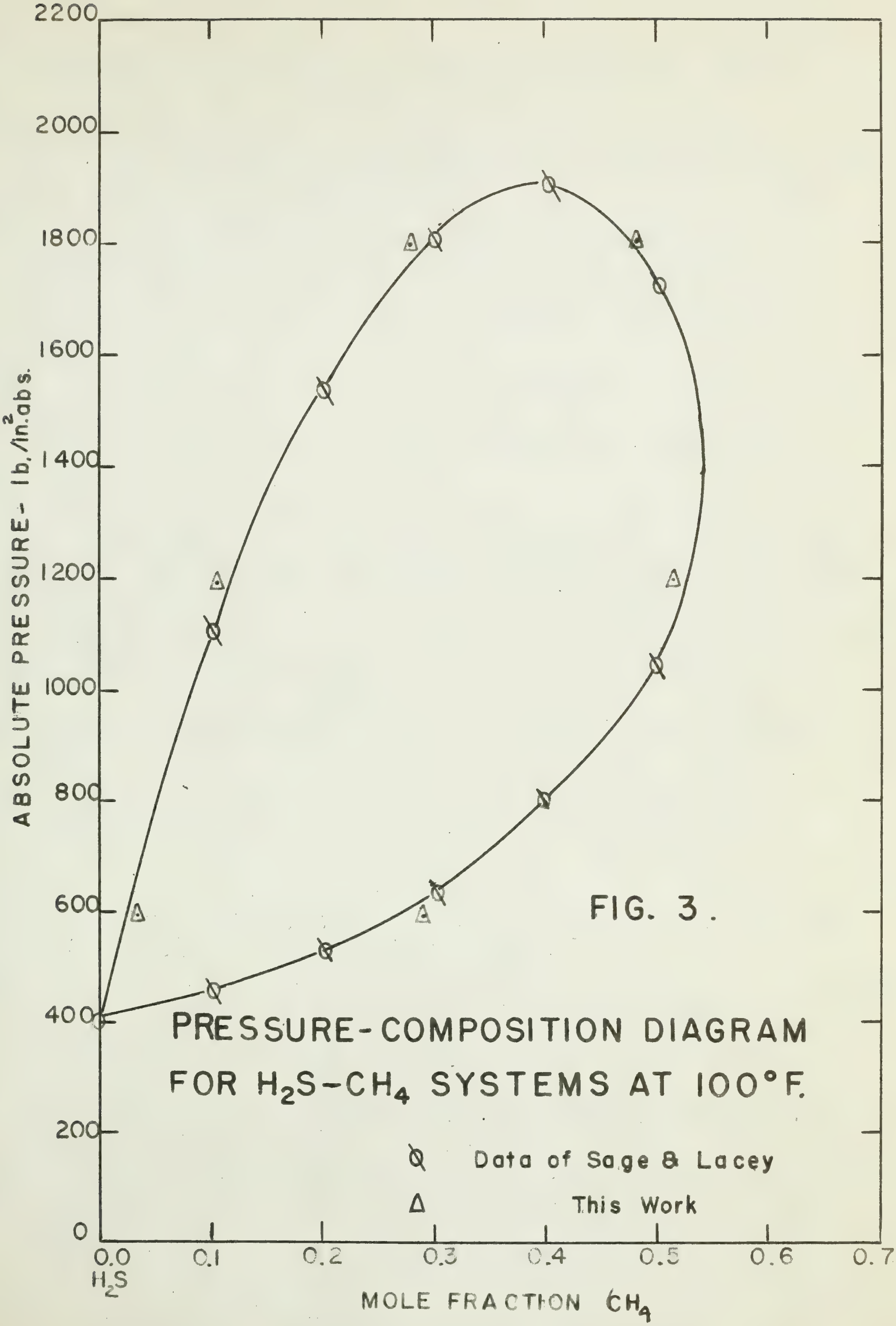


FIG. 3.

PRESSURE-COMPOSITION DIAGRAM FOR H_2S-CH_4 SYSTEMS AT 100°F.

Isobaric sections through the three dimensional phase figure indicate the single state phases and the heterogeneous region as areas, while the phase separating surfaces appear as lines.

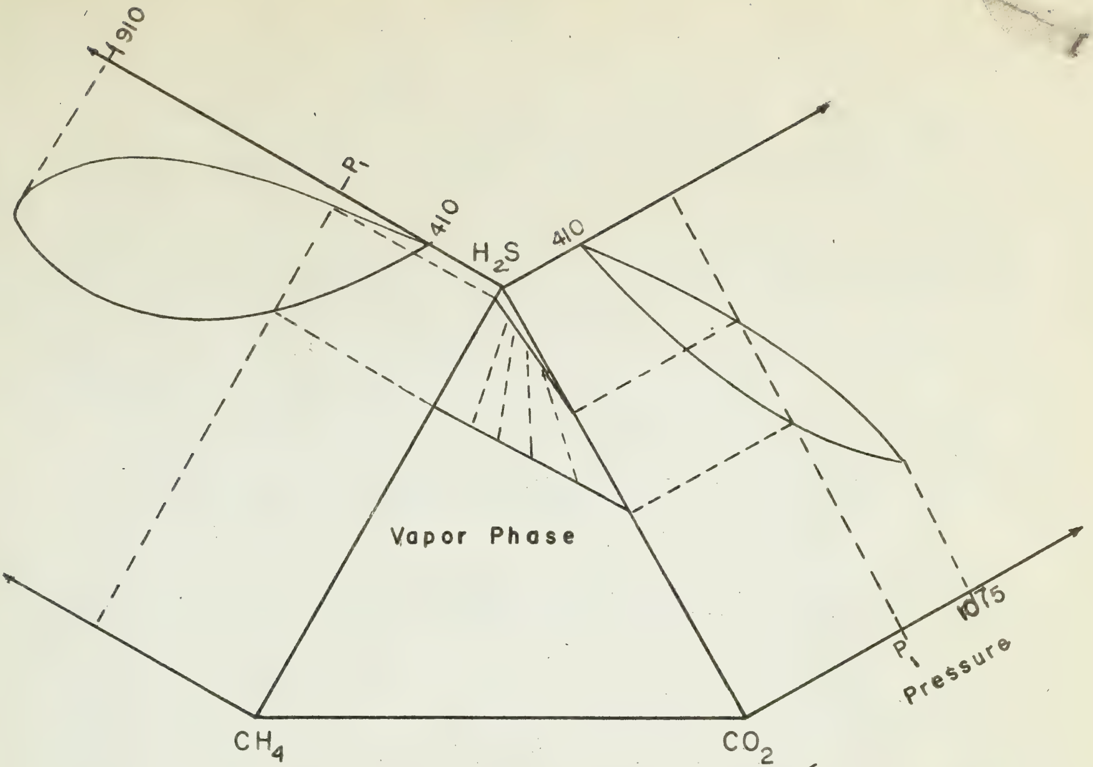
a. Phase Behaviour of Hydrogen Sulfide-Carbon Dioxide-Methane Systems

While the phase rule describes the general nature of the three component phase diagram, more specific information relating to the hydrogen sulfide-carbon dioxide-methane system may be obtained from available data.

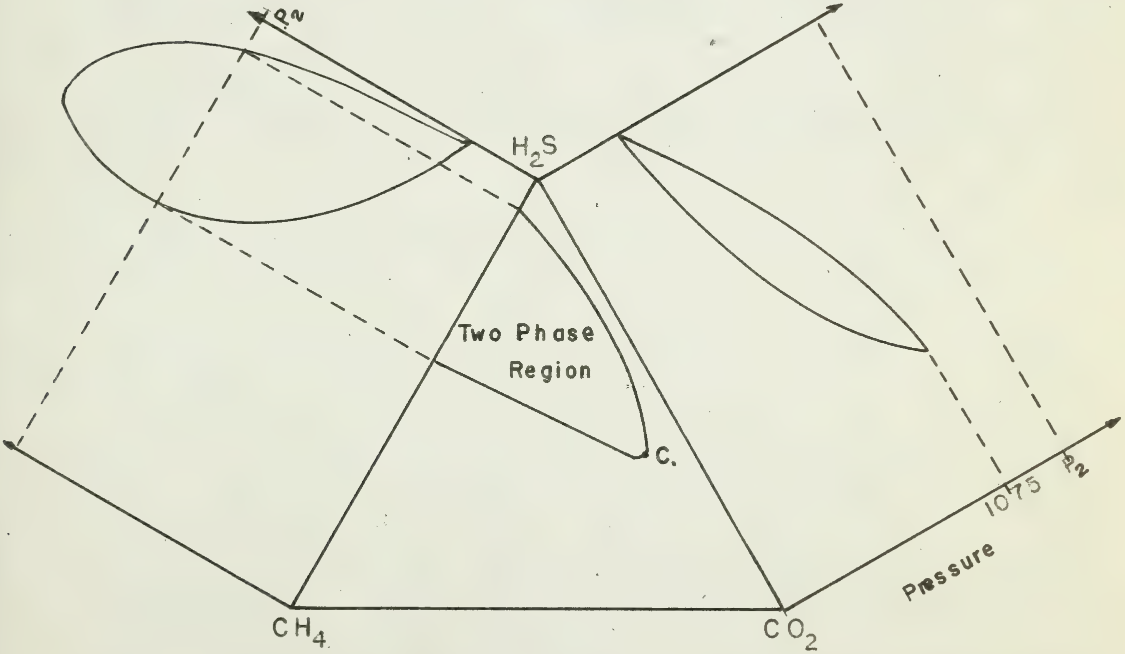
The critical temperature reported for hydrogen sulfide is 212 degrees F.(11), for carbon dioxide is 87.6 degrees F.(15), and for methane is -116 degrees F.(14).

Therefore, at the temperature of 100 degrees F. used during the experimental tests only hydrogen sulfide could exist as a liquid under its vapor pressure of 410 lb/in.^{2}abs. As a result the pressure composition diagrams obtained from the literature at 100 degrees F. indicate the characteristic behaviour of binary systems at temperatures within the binary critical region. The isothermal phase composition sections at the temperatures T_3 and T_4 indicated by Fig.(1) are representative of this behaviour. In this case component B represents hydrogen sulfide while component A represents the more volatile carbon dioxide or methane.

Bierlien and Kay (1) have published phase data for the system hydrogen sulfide-carbon dioxide which was used during the course of this work. Fig.(2) indicates the pressure-composition isotherm for the system at 100 degrees F. This figure was interpolated from the data of Bierlien and Kay at 94 and 105 degrees F. Steckel (1) had published material for the system prior to Bierlien and Kay but the



Part a: Isobaric Section At P_1 Where $410 < P_1 < 1075$ lb./in.^{2} abs.



Part b: Isobaric Section At P_2 Where $1075 < P_2 < 1910$ lb./in.^{2} abs.

FIG. 4.

TERNARY ISOBARIC DIAGRAMS AT 100°F.

highest temperature he investigated was 32 degrees F.

The methane-hydrogen sulfide system was reported in 1951 by Reamer, Sage and Lacey (12) and their phase composition data at 100 degrees F. is indicated by Fig.3. This system and the carbon dioxide-hydrogen sulfide system has been described only in the liquid and vapor phase regions.

Recent work on the carbon dioxide-methane system in the liquid vapor region and at conditions extending to the formation of solid carbon dioxide has been published by Donnelly and Katz(4). This system had been previously investigated by Reamer (10) who determined compressibility factors for gaseous mixtures. However, these binary systems do not exist in the liquid state at 100 degrees F. since the critical temperature of both components is exceeded. So the published data was not directly used in the three component investigations.

The bubble point and dewpoint curves are terminated in both the hydrogen sulfide-carbon dioxide and hydrogen sulfide-methane diagrams at the binary critical points. These represent the maximum pressure at which the heterogeneous regions exist at 100 degrees F. The critical points mark the intersection of the pressure-composition isothermal planes with the critical loci for the two component systems. The critical pressure at 100 degrees F. for the hydrogen sulfide-methane pair is 1910 lb/in.^{2}abs. at a composition of 0.60 mole fraction hydrogen sulfide. The corresponding point for the hydrogen sulfide-carbon dioxide is at 1075 lb/in.^{2}abs. and 0.27 mole fraction hydrogen sulfide.

The hydrogen sulfide-carbon dioxide and hydrogen sulfide-methane pressure composition curves actually represent the termination of the ternary heterogeneous region at the respective pressure-composition sides

of the three dimensional phase diagram. Isobaric ternary composition diagrams therefore intersect the binary pressure-composition boundary curves at pressures within the limits for two phase binary pair existence. The compositions of the two phases in equilibrium for a binary pair are represented at the particular side of the triangular phase diagrams indicating the compositions of that pair.

Two typical ternary isobaric composition diagrams of the type which were expected for the three component system prior to any experimental work are illustrated in Fig.4 part (a) and (b). The diagrams indicate the relationship between the two binary pressure-composition sections and the triangular composition diagrams. The pressure-composition sides of the figure are represented in the same plane as the triangular diagrams for convenience.

Part (a) represents the loci of possible co-existing phases at an intermediate pressure P between the vapor pressure of hydrogen sulfide which represents the lowest pressure at which liquefaction will commence in the system, and the critical pressure of the hydrogen sulfide-carbon dioxide system. The single phase liquid and gas regions are indicated as areas on the diagram extending from the hydrogen sulfide-carbon dioxide boundary curve to the hydrogen sulfide-methane boundary.

Particular systems forming phases in equilibrium have compositions indicated by the intersection of tie-lines with the three component boundary curves.

At pressures above 1075 lb/in.^{2}abs., yet below the critical pressure for the binary hydrogen sulfide-methane system at 1910 lb/in.^{2}abs. the hydrogen sulfide-methane system will form two phases but hydrogen sulfide-

carbon dioxide systems will not. The heterogeneous three component region still exists but no longer extends to the hydrogen sulfide-carbon dioxide axis. It diminishes with increasing pressure eventually merging with the hydrogen sulfide-methane axis at 1910 lb/in.^{2}abs. Part (b) of Fig.4 represents a typical section at a pressure slightly above 1075 lb/in.^{2}abs.

In this pressure range the two surfaces delineating the heterogenous region merge producing a locus of ternary critical points. These extend from 1075 lb/in.^{2}abs at a composition of 0.27 mole fraction hydrogen sulfide for the hydrogen sulfide-carbon dioxide system through a series of three component mixtures to terminate at 1910 lb/in.^{2}abs. at the critical point for hydrogen sulfide-methane at 0.60 mole fraction hydrogen sulfide. The region bounding the heterogeneous zone alters gradually from a dense to a less dense phase, yet as there is no definite demarcation between the two, neither can be defined to be either a liquid or vapor.

5. Idealized Concepts of Phase Equilibria

The quantitative aspects of phase behaviour of liquid-vapor equilibria may be formulated by application of fundamental laws relating to the liquid and vapor states. These relations are based on the concept of idealized gas and liquid states which do not usually exist. Hence the actual values of phase compositions as determined experimentally generally deviate considerably from predicted values. Nevertheless, it is interesting to compare the two.

(a) Dalton's Law

Dalton in 1890 ([illegible]) formulated the general relation which states that the partial pressure of each component in a gas mixture is independent

of the remaining components, depending solely on the quantity of the component and the total pressure. If the gas phase is ideal the partial pressure of a component is equal to the product of the molar proportion of that component and the total system pressure.

$$\text{So:}\quad p_i = Y_i\pi \quad \text{---}\ (3)$$

(b) Raoult's Law

An expression analogous to Dalton's Law has been derived to relate the partial pressure of a component in the gas phase existing in equilibrium with a liquid mixture containing the component. The law formulated by Raoult in 1887 ([illegible]), states that the partial pressure of a component above a homogeneous liquid mixture is equal to the product of the mole fraction of the component in the liquid phase and its vapor pressure at the temperature of the solution

$$\text{Hence:}\quad p_i = X_i P_i^* \quad \text{---}\ (4)$$

Raoult's Law is strictly applicable to an ideal solution only, having no molecular association or chemical combination between the different chemical species in the liquid phase. Molecular diameters must be equal for each component.

Non-ideality is common in the liquid phase, but Raoult's Law is generally applicable without serious error to the solvent portion of the solution.

(c) Ideal Solution Law

Dalton's Law (3) and Raoult's Law (4) may be combined since both expressions yield a common value for the partial pressure of a component present in a vapor phase in equilibrium with a liquid containing the component.

$$\text{Hence:}\quad Y_i\pi = X_i P_i^* \quad \text{---}\ (5)$$

Equation (5) which is termed the ideal solution law, provides a correlation for the distribution of a component between the liquid and gas phases in equilibrium at the system pressure and at the vapor pressure of the component corresponding to the system temperature.

6. Deviations from the Ideal Solution Law

Equation (5) can fail to apply for any component for the following reasons:

(1) Deviations may occur from ideality in the gas phase at certain temperatures and pressures.

(2) Deviations may also occur in the liquid phase due to appreciable molecular association in the dense liquid state even at low pressures.

(3) Vapor pressures are not solely functions of temperature but also increase as the total system pressure increases.

(4) In multicomponent systems the proportions of the component in the liquid and the vapor are dependent on the composition of the remainder of the system. This effect is greatest as system compositions approach a critical point. At the critical conditions $Y_i = X_i$; however, unless the critical pressure is equivalent to the vapor pressure equation (5) will no longer apply.

(5) The vapor pressures for a component no longer exist at a temperature above its critical. Vapor pressures at temperatures above the critical may be obtained from extrapolation of the existing vapor pressure curves, but this procedure is of doubtful validity.

(a) Modification of the Ideal Law

The ideal solution law may be modified for an actual solution exhibiting deviations by the use of a correction factor termed the activity coefficient.

The activity coefficient accounts for all deviations occurring from ideality for a particular component. The resulting equation has the form:

$$Y_i \pi = \gamma_i X_i P_i^* \quad \text{---} \ (6)$$

The value of the activity coefficient is such that equation (6) will apply for component i under the conditions specified. For ideal systems $\gamma_i = 1.0$.

Activity coefficients are best obtained by experimentally determining the proportion of the component in the liquid and gas phases at known pressure and temperature conditions. However, methods based on thermodynamic concepts of equilibria such as the Margules ([illegible]), and Van Laar Equations ([illegible]) ([illegible]) have been developed. The ability to predict activity coefficients would obviate the necessity for experimental phase determination but the utility of the Van Laar and Margules Equations are restricted by the need for experimental data to evaluate particular constants for the equations.

The activity coefficients for the hydrogen sulfide-carbon dioxide-methane system were determined at the test conditions.

(b) Deviation from Ideality in Gas Phase

The gaseous state of matter is considered to exhibit ideal behaviour if the molecules exist as point masses and are without inter-attraction. An ideal gas from the kinetic gas theory will follow the pressure, volume and temperature behaviour predicted by the ideal gas law:

$$PV = nRT \quad \text{---} \ (7)$$

Any real gas exhibits deviations from the gas law but the law is most valid for a gas at conditions furthest from the liquid state. That is, at low pressures and high temperatures.

Other forms of the gas law have been proposed with additional terms to fit the behaviour of actual gases. For engineering purposes, the ideal gas law has been modified by the use of the compressibility factor Z.

Where: $PV = ZRT$ --- (8)

Since compressibility factors are dependent upon pressure, temperature and system composition, experimental pressure-volume-temperature data are required for their determination. This information was obtained during the tests on the three component gas phases.

IV EXPERIMENTAL TECHNIQUES

1. General Methods for Determination of Phase Equilibria

While the general relations governing the pressure-composition behaviour of multicomponent systems may be derived from thermodynamics, no quantitative information for a particular system can be obtained from theoretical considerations alone. Hence each system of interest must be investigated directly. Therefore the aims of contemporary research in the field of phase behaviour are similar, but the types of equipment in use differ considerably. The ultimate purpose of each, however, is to facilitate the control and measurement of the primary phase variables pressure, temperature, and phase composition.

Most methods make use of an equilibrium cell of fixed or variable volume in which the systems are enclosed during the process of achieving equilibrium conditions. The basic differences arise in the design of the cell and its pressure-temperature control, as well as the manner in which phases are removed from it for analysis. The measurement of the pressure, temperature, and volume conditions within the cell at equilibrium differ according to the degree of accuracy desired.

The nature of the pressure and temperature control of the equilibrium cell depends on whether the internal volume is variable or fixed. If fixed, the desired system pressure is achieved by the addition of components in sufficient quantity to achieve the desired pressure. With a fixed cell volume generally no provision is made for direct observations of internal system volume by means of glass sight ports. Hence the entire cell may be heated to the desired level by immersion within an oil-bath without interference of observation. Equipment of this

nature has been used by Boomer (3), and Sage and Lacey (10)(12)(13)(14). The volume of the phases in the cell used by Sage and Lacey was determined by immersion of a heated platinum wire on a vertical movable rod within the cell. Detectable resistance changes occurred within the wire to passage of current due to unequal cooling between phases. The location of the phase interface was readily determined by the position of the rod.

An example of the variable volume, visual type of cell is the equipment used by Professor Katz of Michigan for the carbon dioxide-methane system (4) and described for other hydrocarbon systems (8). Katz uses a cell adapted from a Jerguson Liquid Level Gauge in which pressure changes within the enclosed system are achieved by addition or removal of mercury to the cell contents from a connecting reservoir. Volumetric measurements are made by the use of glass panels in the cell walls allowing direct observation of the cell contents. The cell is heated by immersion in a constant temperature air-bath for elevated temperatures. Another variable volumed cell is that used by Bierlien and Kay for the hydrogen sulfide-carbon dioxide system (1) and described by Kay and Rambosek for the system hydrogen sulfide-ethane (6). It consists of a thick walled glass capillary tube of 2.1 mm. bore. Pressure changes are made with mercury. However, in this case capillary tube is enclosed within a glass jacket and heated by vapors from boiling organic compounds.

Several methods are in use to increase the rate at which equilibrium is approached in the contacting phases. Possibly the simplest, and that which is used by Katz, provides for the agitation of the entire cell. The phases intermingle due to the mixing action of the mercury

and good liquid-vapor contact is achieved. Sage and Lacey use a more complicated spiral agitator immersed within the cell which is rotated by a magnetic drive unit outside the non-movable cell. Bierlien and Kay use a similar arrangement by which a steel shaft is oscillated in the capillary tube by an exterior magnet.

The various techniques are allied in the measurement of the primary phase variables pressure, temperature and composition. For single or binary component systems no phase sampling is required to determine phase composition. In binary system studies a known total composition is made up and compressed to the desired two phase region. The compositions of the resulting phases at equilibrium conditions are then functions of the equilibrium temperature and pressure. However, in ternary or higher systems provision must be made for the phase sampling. Portions of the phases may be removed from sample ports (13) or by the use of adjustable probes within the cell (9). Both phases may also be removed from the cell in their entirety and separated for analysis (4). Generally mercury is added to the cell as the sampling progresses to maintain isobaric conditions.

Pressure intensities within a system are obtained with a calibrated Bourdon tube gauge by Katz. Bierlien and Kay use a Bourdon gauge in conjunction with a dead weight pressure gauge. The dead weight gauge yields more precise results. Sage and Lacey use a pressure balance which is constructed on the principle of the dead weight gauge but is more convenient to use. It is designed in the form of an equal arm balance and suitable weights are added to the balance arm to indicate the pressure.

Temperatures of the heating baths or the equilibrium cells are measured by liquid in glass thermometers (15), or thermocouples (1)(9),

Resistance thermometers are used for the most accurate work (11)(12)(13).

The greatest source of error during phase behaviour studies on multicomponent systems is due to phase samples which are not indicative of the true equilibrium state. Failure to achieve stable equilibrium between the phases prior to sampling may be responsible. During the phase sampling, abrupt pressure changes of a substantial magnitude may occur which destroy the equilibrium. The vapor sampling lines may have become contaminated with liquid during the agitation period or become initially filled with a gaseous portion of the system not at true equilibrium. In such cases the phase samples will be erroneous not yielding a correct result.

These restrictions may be minimized through careful design and proper operational techniques. The experimental data obtained are generally sufficiently worth while for most engineering purposes.

2. Experimental Techniques for the Hydrogen Sulfide-Carbon Dioxide-Methane System

The primary purpose of the experimental program was to define the pressure-composition locus of the two phase boundary surfaces for the three component systems. The pressure range over which two phase equilibrium existed in the system at 100 degrees F. had been determined by the prior work relating to the two component systems but the compositions of the phases in the three component region could not be foretold from existing data.

The experimental method was designed to produce a series of isobaric ternary composition sections for the three dimensional phase figure. At each pressure investigated a series of gas mixtures were prepared having a total composition estimated as being within the heterogeneous region.

The individual gas mixtures were then compressed to the desired pressure and since the overall composition at that pressure was within the heterogeneous region two phases formed. The phase analysis located a point on the liquid and on the vapor boundary surface which were in equilibrium. The series of mixtures at the given pressure fixed the locus of the gas and liquid lines, representing the isobaric intersection of the two phase boundaries. A check on the quality of the experimental results was always obtainable since the liquid, gas and overall system compositions when plotted on the triangular graphs had to lie on a straight tie-line for true equilibrium.

The positions of the phase boundary surfaces over the pressure interval from 410 $lb/in.^2$abs. to 1910 $lb/in.^2$abs. in which two phases exist may thus be located if sufficient isobaric sections are investigated. This experimental work was limited to three sections at pressures of 600, 1200 and 1800 $lb/in.^2$abs. Nevertheless, these data were sufficient to delineate the heterogeneous region.

3. Experimental Apparatus

The equipment was designed so that gas mixtures which were prepared at desired concentrations could be partially liquefied at a particular temperature and pressure. The principal unit of the apparatus comprised the equilibrium cell in which the systems were studied.

Fig.5 is the schematic drawing showing the relation between the main components of the apparatus.

(a) Equilibrium Cell

The phase studies were carried out by use of a variable pressure-volume-temperature cell. In it systems could be raised to a desired temperature and pressure and maintained at these conditions while

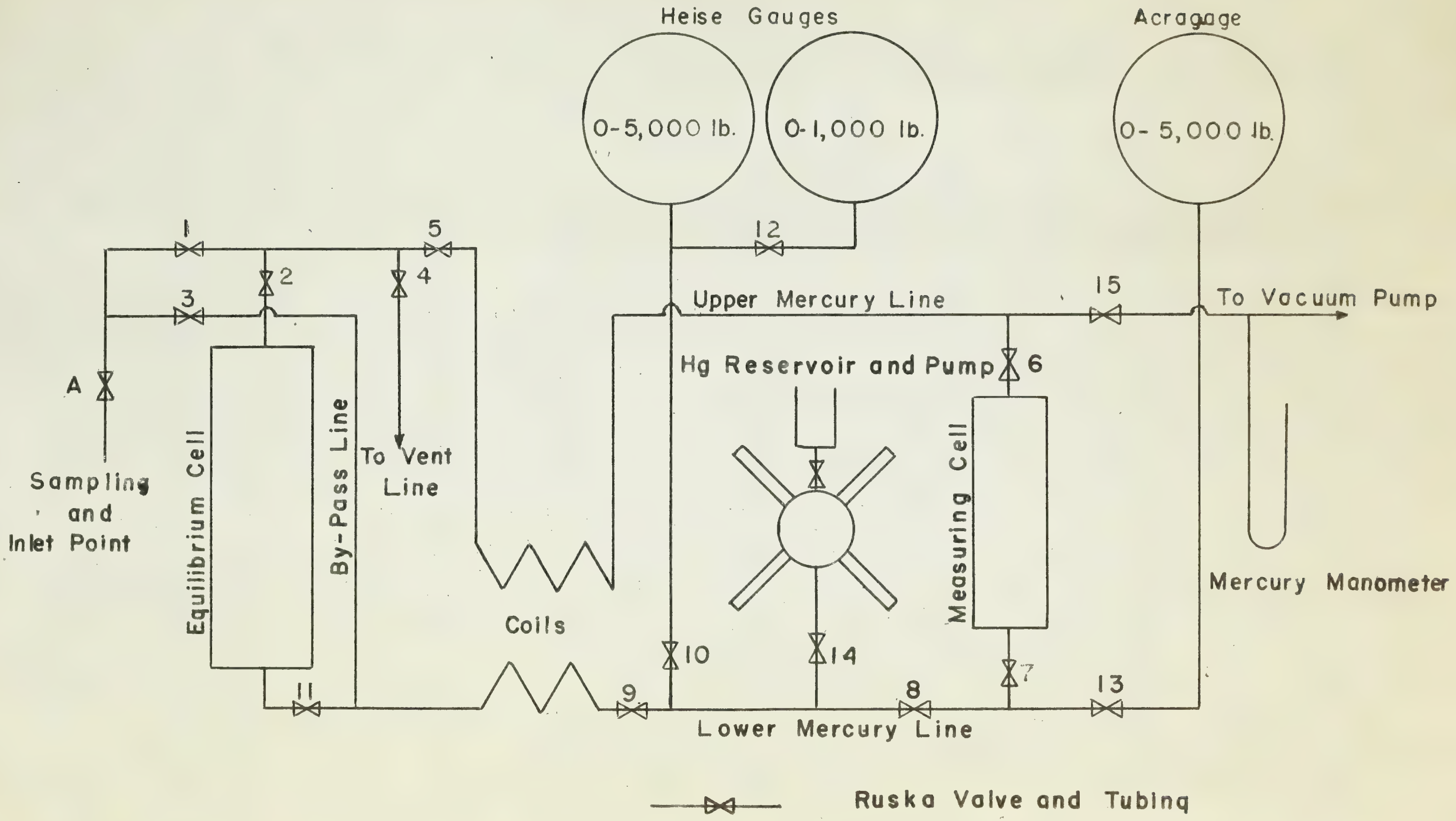


FIG. 5. SCHEMATIC APPARATUS ASSEMBLY

approaching equilibrium. Visual observations of the system were possible since the front and rear faces of the cell were equipped with narrow glass observation ports. The interior volume of the enclosed system was readily varied to achieve a certain pressure by injection or removal of mercury in the cell.

The cell was adapted from a Jerguson Co. Liquid Level Gauge No. 35T40 which was manufactured from type 316 stainless steel. The exterior cell dimensions were 4 in. by 34 in. while the interior cross-section was approximately 1/2 in. by 1/2 in. This gave a total interior volume of approximately 115 cc. The interior was separated into three sections of equal volume connected by ports. The cell was constructed in a laminated form in which three layers of steel were bolted to retain the two layers of safety glass. The sight glass was pyrex 3/4 in. thick with surfaces ground to reduce any visual distortion. The gauge was rated to withstand a maximum pressure of 3,000 lb/in.^{2} at 200 degrees F. and no difficulty was experienced at any time due to leakage past the sealing gaskets. Two stainless steel fittings were specially machined to connect the mercury supply lines to the 1/2 in. N.P.T. female cell connections.

(b) The Air Bath

The cell was permanently mounted within an air bath by 1/2 in. bolts which screwed through the walls of the bath to abutt against the cell. The relative position of the cell within the bath was readily altered by manipulation of the bolts.

The bath was fabricated from 1/4 in. iron plating joined at the corners by 1 in. angle iron. The interior dimensions were approximately 9 in. by 12 in. by 40 in. The interior was lined with 1 1/2 in. of insulation. The front of the bath usually secured by four bolts, was removable to provide access to the cell and attendant fittings. A

safety glass covered opening in the front of the bath, corresponded to the cell visual ports and permitted observation of the cell contents. As a safety feature, a hinged mirror attached to the front allowed the operator to stand to one side of the air bath when making observations.

Two small fans were required to provide a circulation of air within the bath sufficient to maintain isothermal conditions in the air space. The fan motors were mounted on the outside shell of the bath at the top and bottom. The fans were positioned within the bath by means of shaft extensions from the motors.

A lighting system in the bath located behind the visual ports of the cell illuminated the cell interior. Use was made of explosion proof Level Gauge Illuminator No.EPL-51 manufactured by the Jerguson Co. for this purpose. The illuminator consisted of two lights joined to a strip of lucite which diffused the light evenly over the length of the sight port.

The air-bath and the enclosed cell were fastened to a fixed frame by means of trunnions on either side of the bath. A vigorous mixing action between the phases was obtained by rocking the equilibrium cell and its contents through a vertical arc. The rocking motion increased the rate at which composition equilibrium was achieved between the contacting phases and ensured that equilibrium did in fact exist. When not being rocked, the bath was fixed in a vertical position by a catch on the supporting frame.

An interior view of the air bath with the cover removed is indicated by Illustration No. 1. The upper portion of the equilibrium

cell together with the mounting bolts is shown. Illustration No. 2 pictures the complete air bath unit with the cover in place; the entire unit being supported by the mounting frame.

(c) Measurement and Control of the Phase Variables

The important variables in conjunction with phase equilibria which must be kept under rigid control are temperature, pressure, and volume.

(i) Temperatures: The equilibrium cell and its contents were maintained at a uniform temperature by the circulation of heated air in the air bath about the cell. The air was maintained at 100 degrees F. during the test runs by an electric heater consisting of a coil of nichrome wire mounted by insulators on the sides of the bath. Current amperage to the heater was regulated with a Variac type variable potential source. System temperatures were maintained at a constant level by on - off control of the heating circuit, provided with a thermostat for this purpose. An American Instrument Co. bimetallic thermostat No. 4-235 was located on the top of the air-bath with the temperature sensitive element immersed in the air-bath. The thermostat operated in conjunction with an American Instrument Co. Electronic Relay No. 4-5301 which actuated the heater circuit. The combination provided sensitive regulation without temperature cycling. Temperatures within the bath did not vary more than 0.5 degrees F. from top to bottom at any time. The heavy walled construction of the cell gave it a high heat capacity aiding the maintenance of isothermal conditions.

The temperature level of the cell was measured with three copper-constantan thermocouples embedded 1/2 in. within the wall of one side

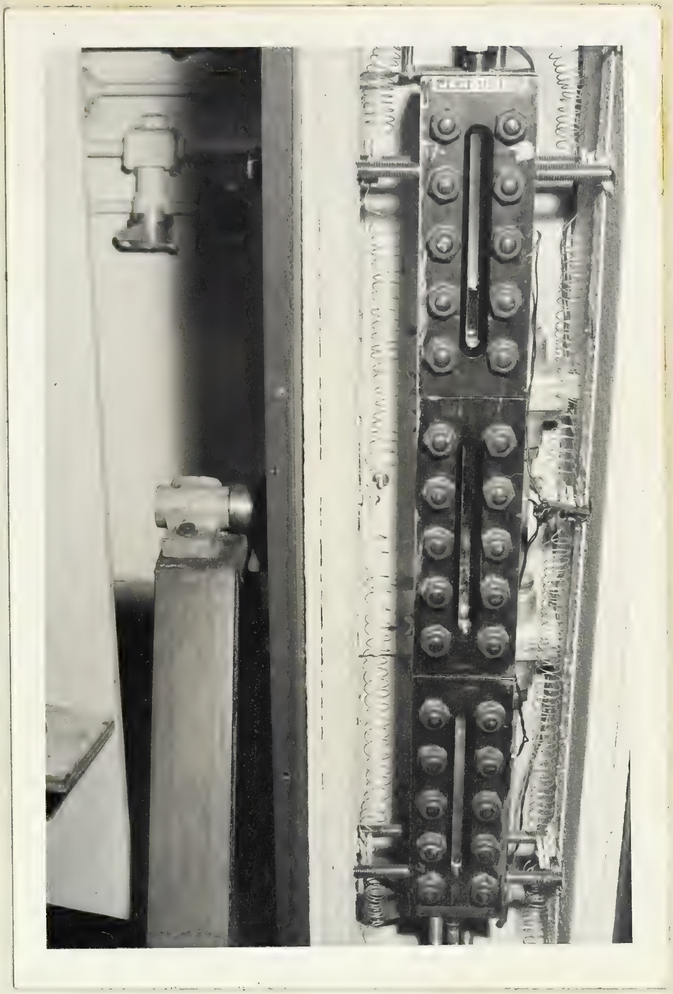


Plate 1: Equilibrium Cell and Air Bath

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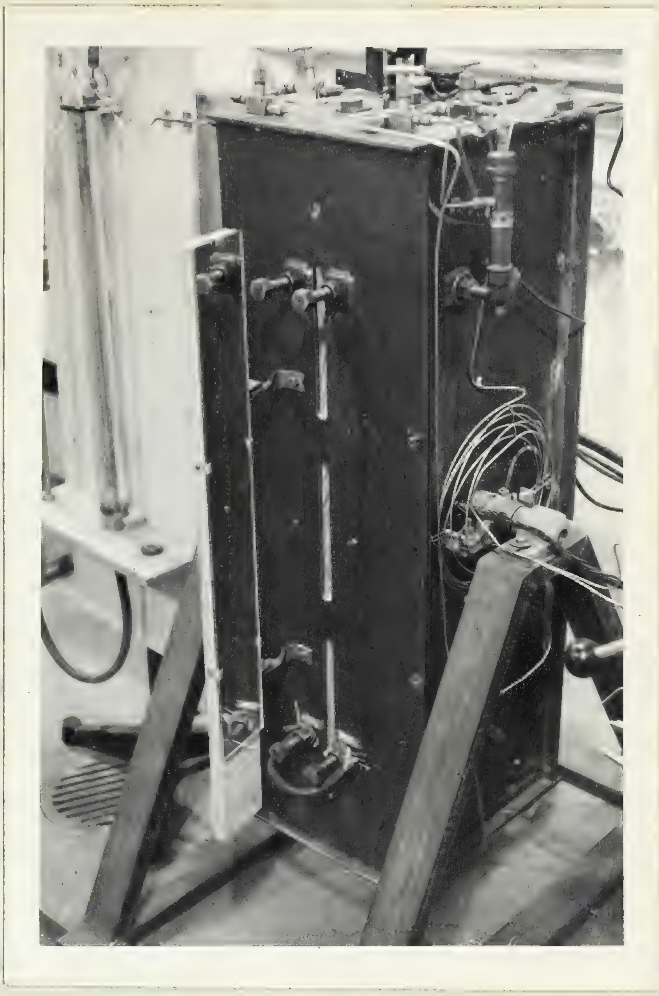

Plate 2: Air Bath

of the cell and located equidistantly along the cell. Two additional thermocouples at the top and bottom of the air space indicated air bath temperatures. The thermocouples leads were joined to a multiple position switch which connected any particular thermocouple junction to the Leeds and Northrup Potentiometer used during the runs. All thermocouple cold junctions were at the ice-point.

(ii) Pressure: The desired pressure in the equilibrium cell was achieved by reducing the volume of the confined system using mercury injection from a mercury pump. Mercury was used as the pressurizing medium since it possessed the desired qualities of inertness, low vapor pressure and incompressibility.

The mercury pump was manufactured by the Ruska Instrument Co., and was rated to withstand 10,000 lb/in.^{2} internal pressure. The pump was hand-operated, mercury being forced into the lines by positive displacement from a screw actuated plunger within the pump barrel. The pump was volumetrically calibrated having a total volume of 250 cc. Additional mercury as needed was added to the pump from a connecting reservoir.

Pressures within the system were recorded by Bourdon-tube pressure gauges. The indicated gauge pressures were corrected to absolute pressures by allowances for atmospheric pressure and for the heads of mercury between the gauges and the point in the system at which the pressure was desired. Care was taken during the test to ensure that at all times the Bourdon-tubes and connecting lines were full of mercury. Two gauges manufactured by the Heise Gauge Co. and rated at 1,000 lb/in.^{2} and 5,000 lb/in.^{2} were used. The serial numbers of these gauges were H4441 and H3272 respectively. The 1,000 lb/in.^{2} gauge had 2 lb. subdivisions and the 5,000 lb/in.^{2}

gauge had 10 lb. subdivisions.

At system pressures below 1,000 lb/in.^{2} the lower range gauge was exclusively used since it was possible to obtain more accurate pressure readings due to the small pressure subdivisions. A third Acragage type gauge capable of recording to 5,000 lb/in.^{2}abs. was also utilized for pressure measurements above 1,000 lb/in.^{2}abs.

Prior to use the Heise Gauges had been calibrated by dead weight testers from the Department of Chemical and Petroleum Engineering and The Conservation Board Laboratory at Devon, Alberta. The calibration curves are indicated by Fig.22, Appendix II.

(iii) System Volumes: All system volumes were indirectly obtained from the elevations of the appropriate fluid interfaces which were then referred to a permanent datum elevation marked on the equipment. The differences in height were used in conjunction with volumetric calibration curves. The system elevations were measured with a cathetometer which could be read to 0.1 mm. The cells had been volumetrically calibrated by the mercury pump with respect to the datum elevation prior to the experimental work. The calibration curves for the equilibrium cell and the measuring cell are represented by Fig.23 Appendix II. While the mercury pump was provided with a volumetric scale it was only useful for determining quantities of mercury displaced from it rather than total volumes. Hence use of a cathetometer was necessary.

(d) The System Measuring Cell

The second major portion of the equipment pertained to the method whereby system compositions were made up to a requisite specification. Components had to be added in known amounts to the equilibrium cell to prepare a desired gas mixture.

Three additional Jerguson Cells with sight ports were provided for this purpose, although only one was actually used. The others were retained as potential storage receivers for systems of known composition. During the preparation of a system the components were separately added to the measuring cell and the appropriate pressure, volume and temperature measurements were made to determine the molar quantity prior to injection of the component into the equilibrium cell.

The total capacity of the measuring cell was approximately 120 cc. The internal volume was varied by mercury displacement with the mercury pump and internal pressures were indicated by the pressure gauges. Volumes were measured by use of the cathetometer.

The cell was not temperature regulated but was exposed to the ambient room air temperature. Since the heat capacity was high and the room temperature fairly uniform, no significant temperature changes occurred during the measurement of a component. The temperatures were obtained by use of a thermocouple in the cell.

(e) Assembly of Apparatus

All major components except the equilibrium cell and air bath were mounted on a Dexion frame. This included the mercury pump, measuring cells and connecting tubing. The pressure gauges, electrical switches together with the heating circuit equipment were fastened on a plywood panel board.

A Cenco-Hyvac Vacuum Pump and a mercury manometer to indicate the degree of vacuum were also mounted on the Dexion frame. The vacuum pump was necessary to evacuate residual gases from the system prior to an experimental run and to provide a vacuum source for the sampling operation.

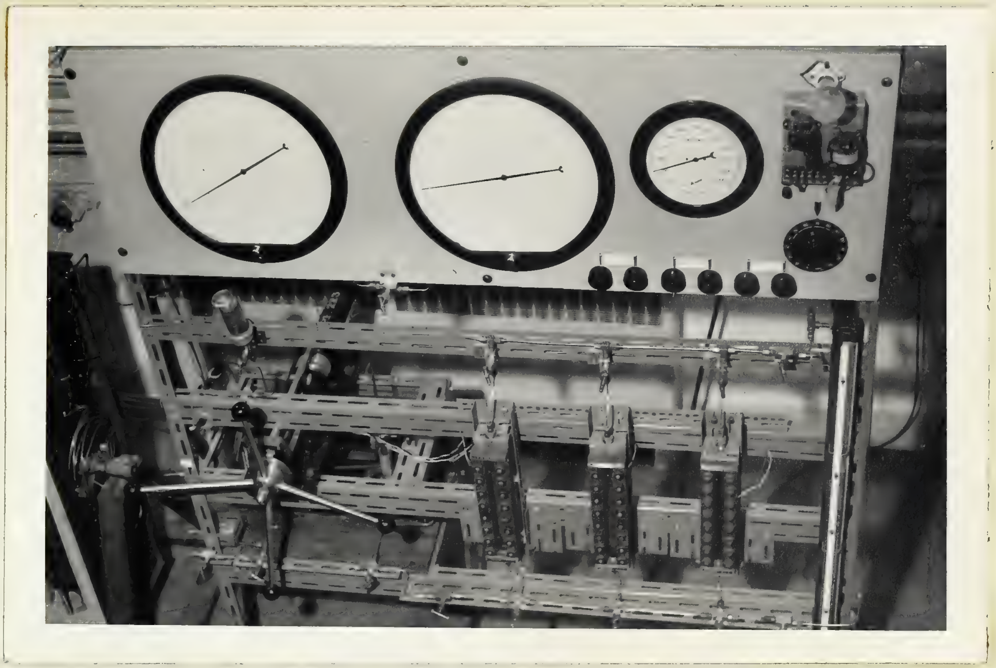

Plate 3: Panel Board

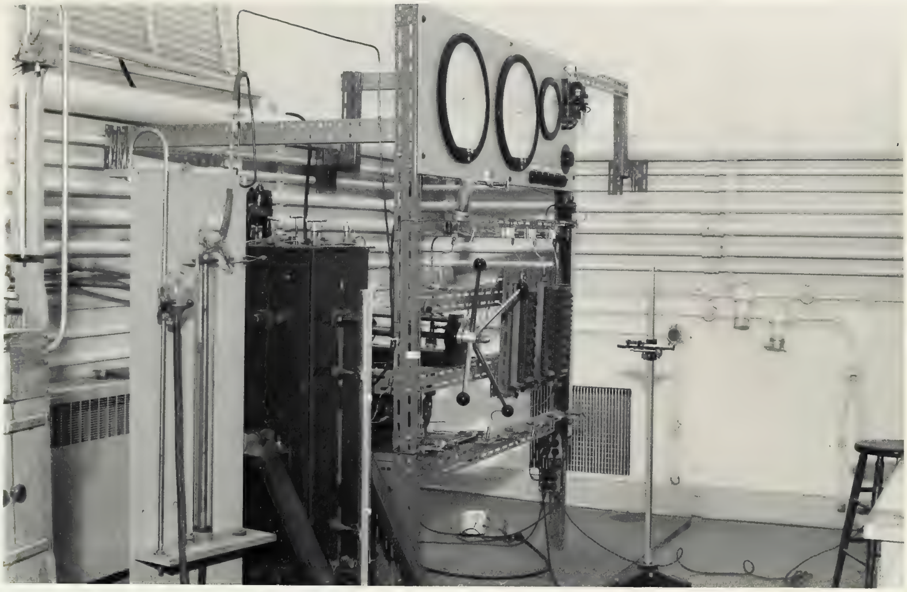

Plate 4: Experimental Apparatus

Illustration No. 3 provides an oblique view of the supporting frame together with the mounted units, tubing and valving. The upper portion of the frame comprises the panel board with the pressure gauges and electrical equipment. Illustration No. 4 gives an overall view of the entire experimental apparatus.

All the high pressure units were connected by stainless steel tubing obtained from the Ruska Co. The tubing, 1/8 in. o.d. and 1/16 in. i.d. was rated to withstand 15,000 lb/in.^{2}abs. radial pressure. All tubing connections were made by compression type joints requiring special flaring of the tube ends. The two lines to the air bath were wound in coils on the air bath to permit its movement during the phase agitation.

The stainless steel needle valves used on the high pressure lines were also manufactured by the Ruska Co. and had hardened needle tips and seats. Teflon O-ring packing was used in the packing glands. Some difficulty was experienced due to failures at the tips of the needles after repeated valve operation. Special Ruska coned fittings were used to connect the tubing and valves.

Since all portions of the equipment in contact with the mercury and hydrogen sulfide were stainless steel, no corrosion difficulties were encountered.

4. Safety Precautions

The chief hazards encountered during the equipment operation were as a result of the high pressures and the poisonous nature of hydrogen sulfide. The former was minimized as much as possible by the enclosure

of the equilibrium cell within the heavy-walled air bath. The mirror used on the air-bath also permitted indirect vision of the system without direct exposure. The pressure gauges were located above direct eye-level on the panel board to reduce danger arising from failure of the Bourdon tubes.

All the equipment was located in the High Pressure Laboratory of the Engineering Building in Room 101. The laboratory was specially designed for work of this nature, being provided with windows of segmented safety glass which would not shatter in the event of an explosion. Also sparking hazard was reduced by the use of safety electrical wall outlets.

The problem of air pollution with hydrogen sulfide was more serious but was partially overcome by the installation of a 3,000 cu. ft./min. capacity fan located in a window directly behind the apparatus. A gas mask was also available had the toxic concentration in the air become lethal. All systems were discharged from the equilibrium cell at the conclusion of test runs through a 1 in. pipe which vented outside' the building.

5. Materials Used

The hydrogen sulfide used was supplied by the Matheson Co., East Rutherford, N.J. The purity was reduced by the presence of small amounts of organic compounds together with nitrogen and carbon dioxide. An analysis of a typical gas portion was supplied by the manufacturer as being:

	Mole %
Hydrogen sulfide	98.8
Methylene chloride	0.4
Methyl Mercaptan	0.3
Nitrogen	0.2
Carbon Dioxide	0.3

Gas phase chromatography tests on the gas from the cylinder indicated a trace of carbon dioxide which was within the 0.3% limit specified by the manufacturer. The presence of carbon dioxide in the hydrogen sulfide was not too serious, but in an effort to reduce it and any non-condensable nitrogen still further, all the hydrogen sulfide was removed from the cylinder in the liquid phase.

Carbon dioxide was prepared by Liquid Carbonic Co., Ltd., Edmonton and was guaranteed to be 99 mole % impurity.

The methane was supplied courtesy of the Phillips Petroleum Co., Bartlesville, Ont., and was of special research grade being 99.8 % purity. No attempt was made to further purify the carbon dioxide or methane.

The carbon dioxide and methane were also tested by gas phase chromatography which failed to reveal any detectable impurities.

V. EXPERIMENTAL RESULTS

1. Experimental Phase Equilibrium Data

The experimental determination of phases in equilibrium at the pressures of 600, 1200 and 1800 lb/in.^{2}abs. are recorded in Tables 1, 2 and 3 respectively. The tables are in Appendix I. The isoberic composition plots for these pressures are indicated by Figs.6, 7 and 8.

In most cases the liquid, vapor and overall compositions were connected by straight tie-lines. If variations from linearity among the three plotted points did occur, the tie-lines were located through the vapor phase and overall system compositions. It was felt these points were more likely to be correct than the liquid locus which was the most difficult of the three to obtain accurately. Generally, no significantly large error was noted, most points being within the maximum deviation of 1% which could be attributable to the analysis procedure.

(a) Phase Compositions at 600 lb/in.^{2}abs.

The 600 lb/in.^{2}abs. series of data were taken to determine the shape of the liquid-vapor region at a pressure below the critical pressure of the hydrogen sulfide-carbon dioxide system yet to be within the liquid formation region above the vapor pressure of hydrogen sulfide. In this pressure range the heterogeneous area extends across the isobaric composition diagram between the hydrogen sulfide-methane and hydrogen sulfide-carbon dioxide binary composition axes.

The best fit line through the liquid compositions was straight, connecting the two liquid compositions for the binary pairs. That for the vapor locus was nearly straight except for a trend extending from 10% carbon dioxide to 25% carbon dioxide in the gas phase, in which the

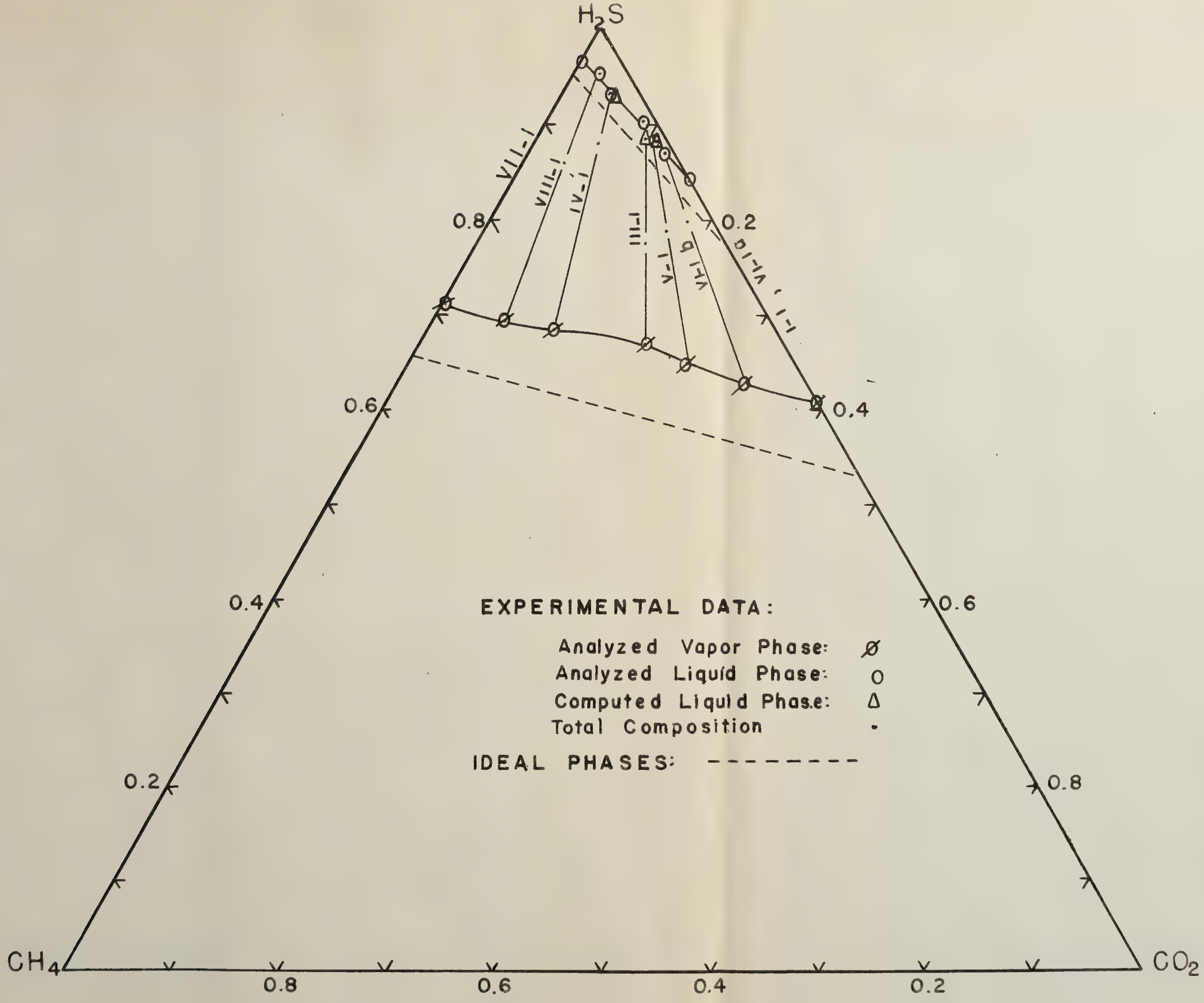

FIG. 6: MOLAR COMPOSITION DIAGRAM
T = 100 °F ; P = 600 lb./in.^{2} abs.

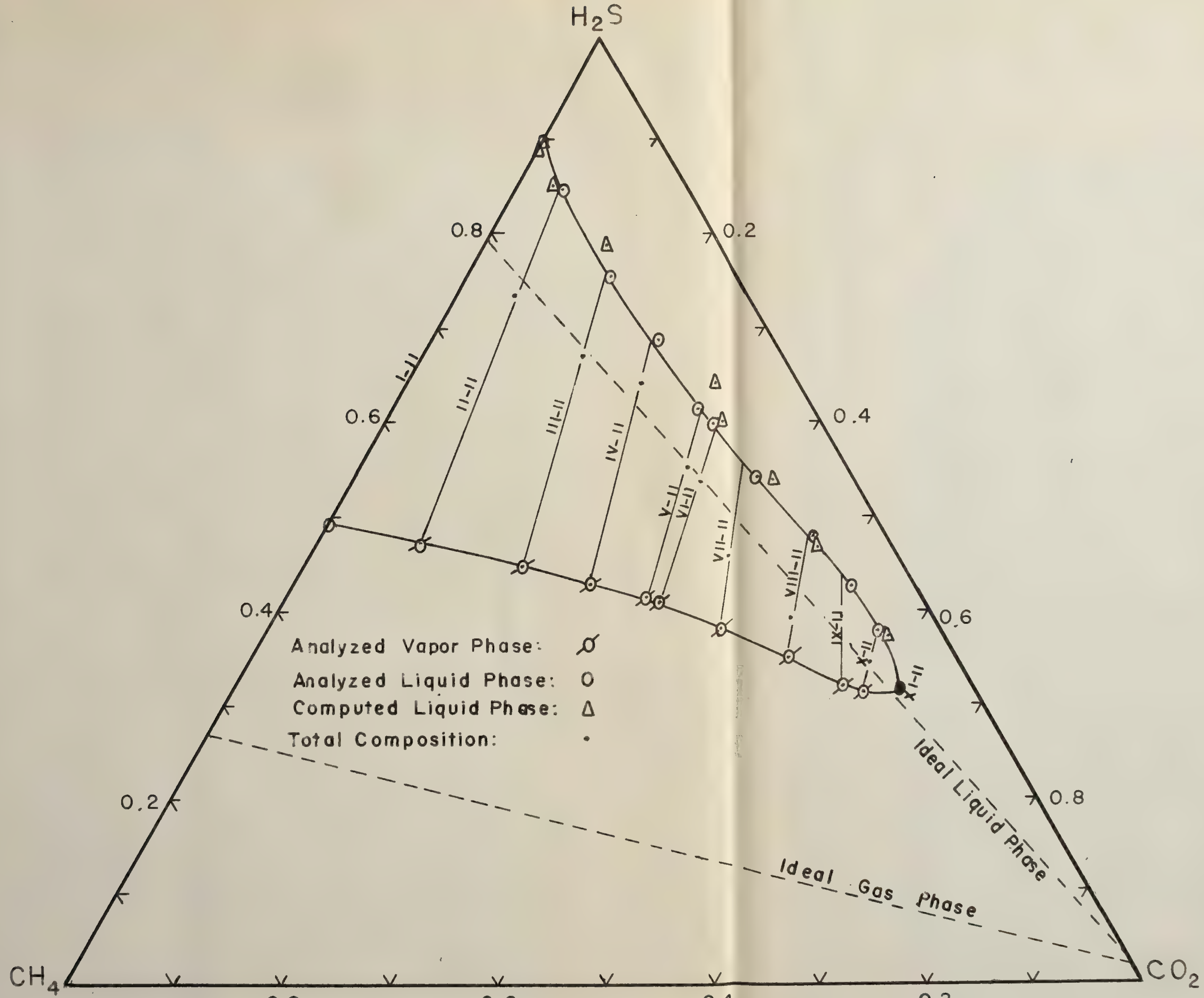

FIG. 7 MOLAR COMPOSITION DIAGRAM

T = 100°F ; P = 1200 lb./in.^{2} abs.

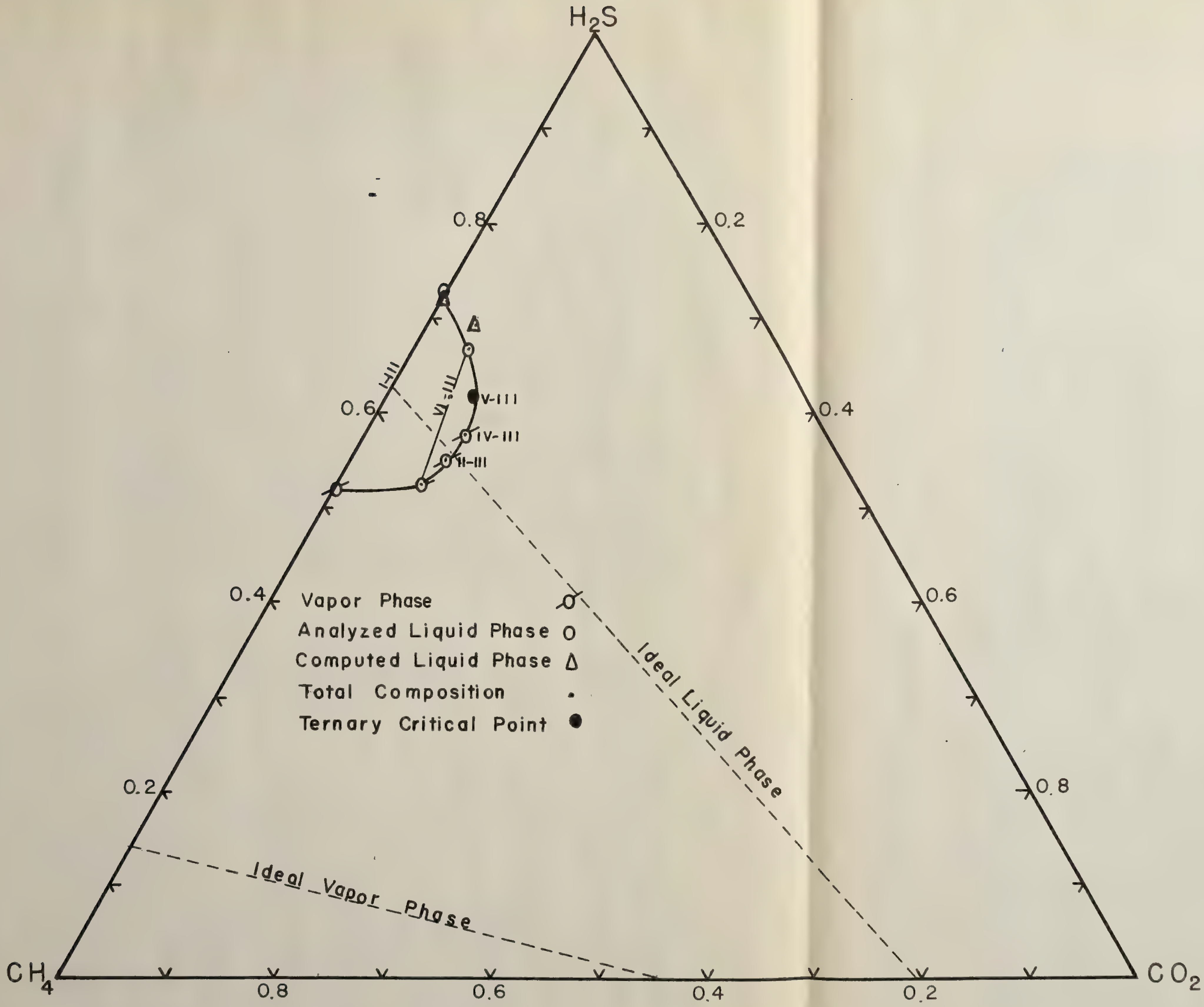

FIG. 8: MOLAR COMPOSITION DIAGRAM

T = 100° F. ; P. = 1800 lb./in.^{2} abs.

line moved slightly into the heterogeneous two-phase region.

(b) Phase Compositions at 1200 lb/in.^{2}abs.

The isobaric phase diagram Fig.7 gives phase relationships for the ternary system at a pressure slightly above the critical pressure of the binary pair hydrogen sulfide-carbon dioxide. The shape of the boundary curves are again fairly linear, however both curves do indicate a slight movement of the phase surfaces into the heterogeneous region. The boundaries merge rather sharply at the ternary critical point for 1200 lb/in.^{2}. The critical point is in fairly close proximity to the hydrogen sulfide-carbon dioxide axis since the ternary critical pressure is only 173 lb/in.^{2}. higher than the binary system critical pressure.

Although a dense and less dense phase exists in the region of the critical point, one merges into the other so that it is not possible to define either state as being a liquid or gas. Most investigators somewhat ambiguously term this region to be existing as a fluid state.

(c) Phase Compositions at 1800 lb/in.^{2}abs.

The volume of the heterogeneous region steadily decreases in magnitude as pressures increase from the hydrogen sulfide-carbon dioxide. critical pressure to the hydrogen sulfide-methane critical pressure. This decrease is reflected in a retreat of the phase surfaces to the hydrogen sulfide-methane axis of the ternary phase diagrams with increasing pressure.

The 1800 lb/in.^{2}abs. diagram Fig.8 graphically indicates the diminution in the heterogeneous area from the area which existed at 1200 lb/in.^{2}abs. At the pressure of 1910 lb/in.^{2}abs., which is the critical pressure of the hydrogen sulfide-methane system, the area

would vanish entirely at 0.27 mole fraction hydrogen sulfide.

The nature of the boundary curves was adequately portrayed by only one three component system in the heterogeneous area. At 1800 lb/in.^{2}abs. the boundary surfaces are no longer flat but curve into the critical point.

(d) Comparison of Binary System Data with Published Values

The liquid and vapor compositions for the binary hydrogen sulfide-methane systems determined experimentally at 600, 1200, and 1800 lb/in.^{2}abs. agree quite well with the data published by Sage and Lacey (11) at 100 degrees F. Both sets of binary data are shown by Fig.3.

The Bierlien and Kay data for the hydrogen sulfide-carbon dioxide binary pairs could be checked only at the 600 lb/in.^{2}abs. tests. The experimental liquid composition agrees quite well as indicated by Fig.2, but the vapor phase is 5% richer in carbon dioxide than the value indicated from the data of Bierlien and Kay. Several experimental determinations were made at 600 lb/in.^{2}abs., which all agreed within 0.5%, so the discrepancy could not be attributable to experimental error. The difference could be due to the necessity of having to interpolate between experimental data reported by Bierlien and Kay.

(e) Comparison of Calculated and Analysed Phase Compositions

Whenever possible the composition of the liquid phase for a run was calculated by the method outlined in Appendix III. This procedure had been initially intended to supplant the direct analysis of the liquid phase. However, the accuracy of the calculation depended on the gas phase analysis and the computed total system composition together with certain volumetric measurements made on the system at the equilibrium

conditions. Since all three quantities were subject to the normal errors of measurement, it was not surprising that in general rather poor agreement existed between the calculated liquid compositions and the values indicated by the tie-line positions through the vapor and total mixture compositions.

2. Description of the Critical Phenomena

Interesting visual changes occurred in the liquid and vapor phases during the transition interval from total system compositions within the three component heterogeneous region to the critical locus. These changes were observed through the glass-windowed cell for the runs at 1200 and 1800 lb/in.^{2}abs.

The interface between the phases became progressively flatter as the critical locus was approached. The meniscus altered from the typical concave surface of a solid wetting liquid to a hairline interface which was nearly indiscernible. Also the fluidity of the liquid phase during phase agitations was noted to increase. Both changes were indicative of the decrease in surface tension and viscosity of the liquid phase as it approached a state akin to that of a vapor.

The mechanical agitation of systems near the critical caused an extreme ebulition action to occur. This destroyed any visible differences between the phases leaving the system as a finely dispersed translucent white fog. This state continued for a brief period after cessation of agitation while the phases slowly reformed. The phase separation occurred from the mercury interface upward for the more dense phase and from the top of the cell downward for the less dense. The resulting interface remained indistinct for a considerable period of time from the action of numerous tiny bubbles circulating throughout

the liquid phase and droplets slowly falling from the vapor phase.

Any small abrupt pressure reductions near the critical locus would destroy the equilibrium disrupting the liquid phase so violently into the vapor that the entire system would momentarily appear black due to interference with light transmission through the cell. This extreme pressure sensitivity which was noted only in the critical regions, increased the difficulty of the sampling operation to a considerable extent.

At the particular system compositions of runs XI - II and V - III color phenomena were noted. These compositions as listed in Appendix I, were assumed to be the ternary critical points for 1200 and 1800 lb/in.^{2}abs. respectively.

At all other compositions within the heterogeneous region the phases were clear and colorless, but at the critical points a definite color change was noted. At pressures ten to fifteen lb/in.^{2} above the equilibrium pressure, the single phase fluid assumed a translucent yellow appearance. As the pressures were gradually lowered, the color of the phase intensified into amber while still remaining in the single phase. The system would be a reddish-orange at the equilibrium pressure whereupon a pressure drop of approximately 1 lb/in.^{2} would cause a phase separation. The more dense phase formed occupied nearly 80% of the total system volume. The meniscus was nearly indistinguishable due to the dark color and the vigorous boiling action at the interface. As the pressures were further lowered the proportion of the dense phase decreased as did the color intensity.

The nature of the color phenomenon was similar at both pressures. However, the color effect was more intense at the higher pressure.

The critical color phenomenon was first described by Altschul in 1895 (7) and more thoroughly studied by Travers and Usher in 1906 (7). The tendency of a critical system to produce a reddish color to transmitted light and a bluish appearance to reflected light is thought to be due to alteration of the refractive index by the formation of small surfaces in either phase due to transference of portions of one phase to the other. At the critical condition, the surface tension of the phase separating meniscus is very low and could readily permit the passage of small quantities of either phase through it to exist in a stable form in the other phase.

3. Correlation of Experimental Data

The compositions of the phases for the test mixtures at the pressures studied together with the resulting tie-lines were located at random intervals on the ternary composition graphs. The reason for this was that the overall system compositions could not be predetermined to yield definite liquid and vapor compositions. However, it was desirable to locate additional tie-lines at regular composition intervals in the heterogeneous areas for each ternary diagram. These tie-lines could then be used to correlate the behaviour of corresponding systems at different pressures.

The additional tie-lines were plotted on the vapor phase boundary lines at even values of a parameter C which is defined by the ratio: $\frac{Y_1}{Y_1 + Y_3}$. The terminating position of the tie-lines on the liquid phase line were determined by interpolation of the tie-lines between existing experimental tie-lines.

This method of locating corresponding tie-lines for different isobaric phase diagrams in ternary systems has been described by

Billman, Sage and Lacey (2) for the system: methane, propane and n-pentane.

(a) Experimental Equilibrium Constants

Equilibrium constants are commonly used to express the relationship between liquid and vapor phases in equilibrium. The equilibrium constant is defined as the ratio of the mole fraction of the component in the vapor phase to the mole fraction in the liquid phase, that is:

$$K_i = \frac{Y_i}{X_i} \quad \text{---} \ (9)$$

By definition the equilibrium constant for a given component is a function of temperature, pressure and composition. The experimental phase composition data were utilized to calculate equilibrium constants for the three components.

With the three isobaric phase diagrams the composition of co-existing phases were determined as fixed by the tie-lines at even values of the parameter C ranging from 0 to 1.0. The values of K were then directly obtained for these compositions and are reported in Tables 4 and 5 Appendix I. together with the compositions of the phases. The best fit plots for each component indicate the effect of pressure on the equilibrium constants for each particular value of C. The equilibrium graphs for hydrogen sulfide are shown in Fig.9 for methane in Fig.10 and carbon dioxide in Fig.11.

The boundary equilibrium curves at C equal to zero and unity representing the binary hydrogen sulfide-methane and hydrogen sulfide-carbon dioxide systems respectively, were determined from the published data at pressures intermediate to the ones studied. No border equilibrium curve could be determined for carbon dioxide at the C parameter equal to zero or for methane at a C Value of unity since these respective

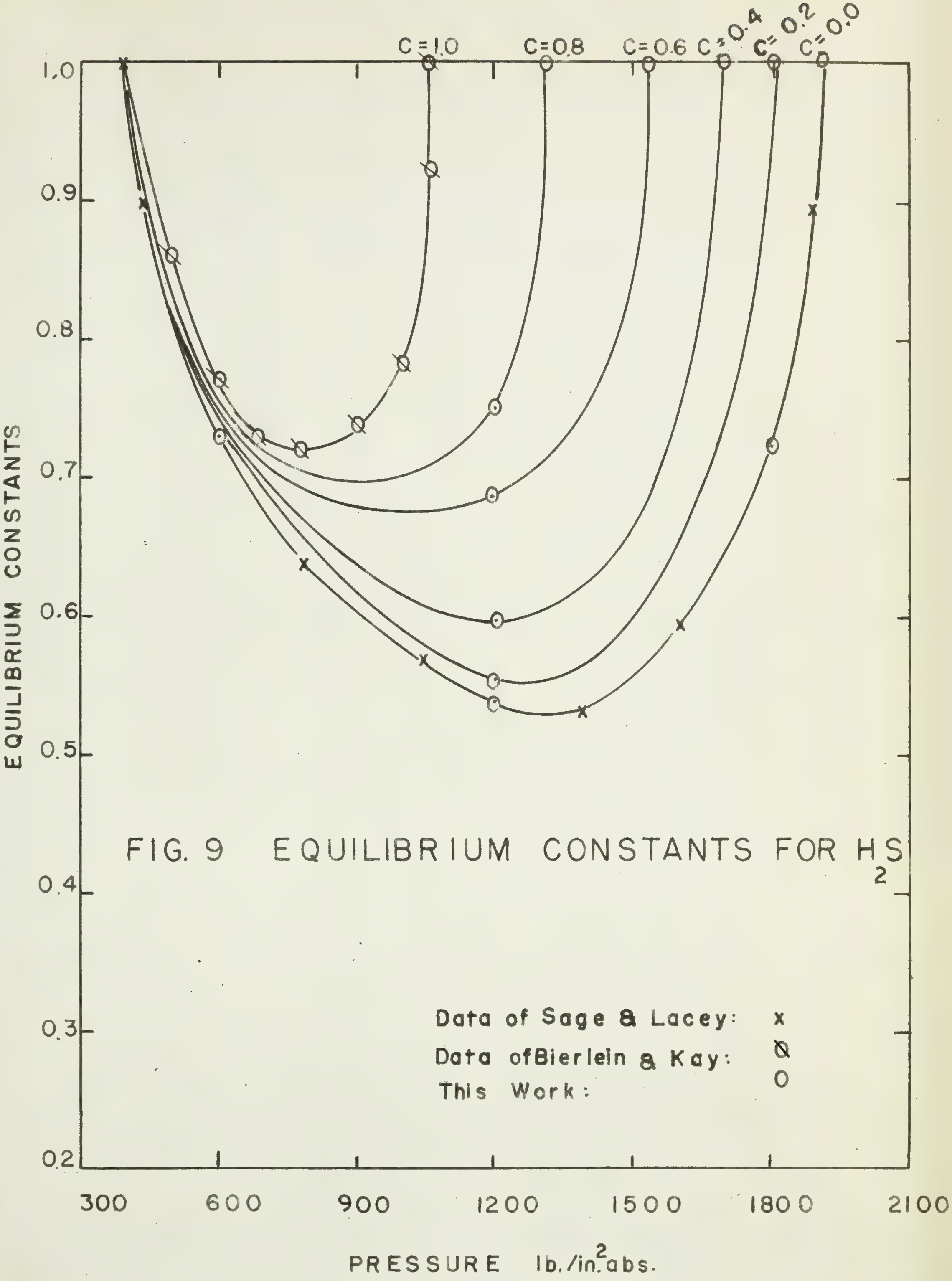

FIG. 9 EQUILIBRIUM CONSTANTS FOR H_2S

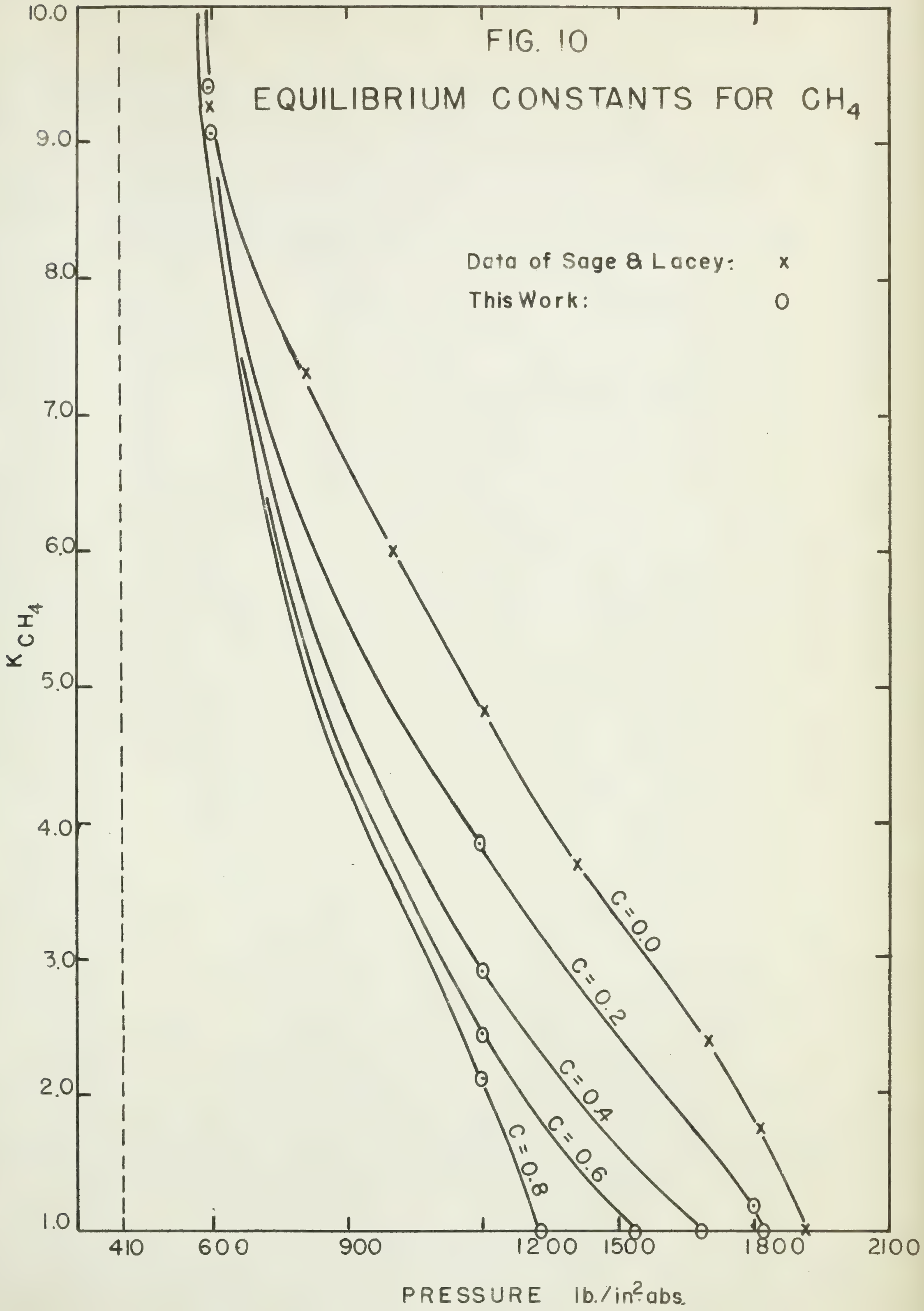

FIG. 10

EQUILIBRIUM CONSTANTS FOR CH_4

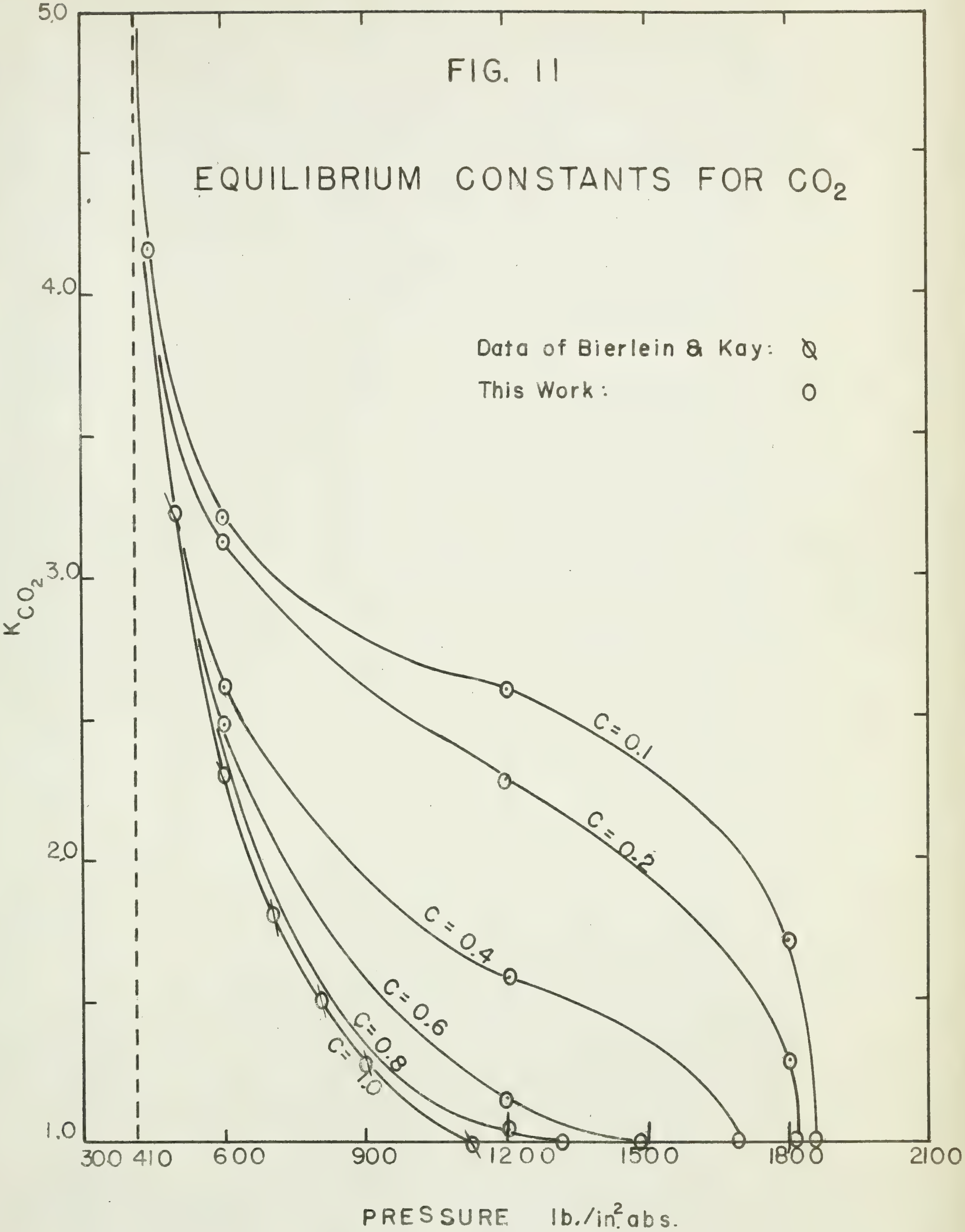

FIG. 11

EQUILIBRIUM CONSTANTS FOR CO_2

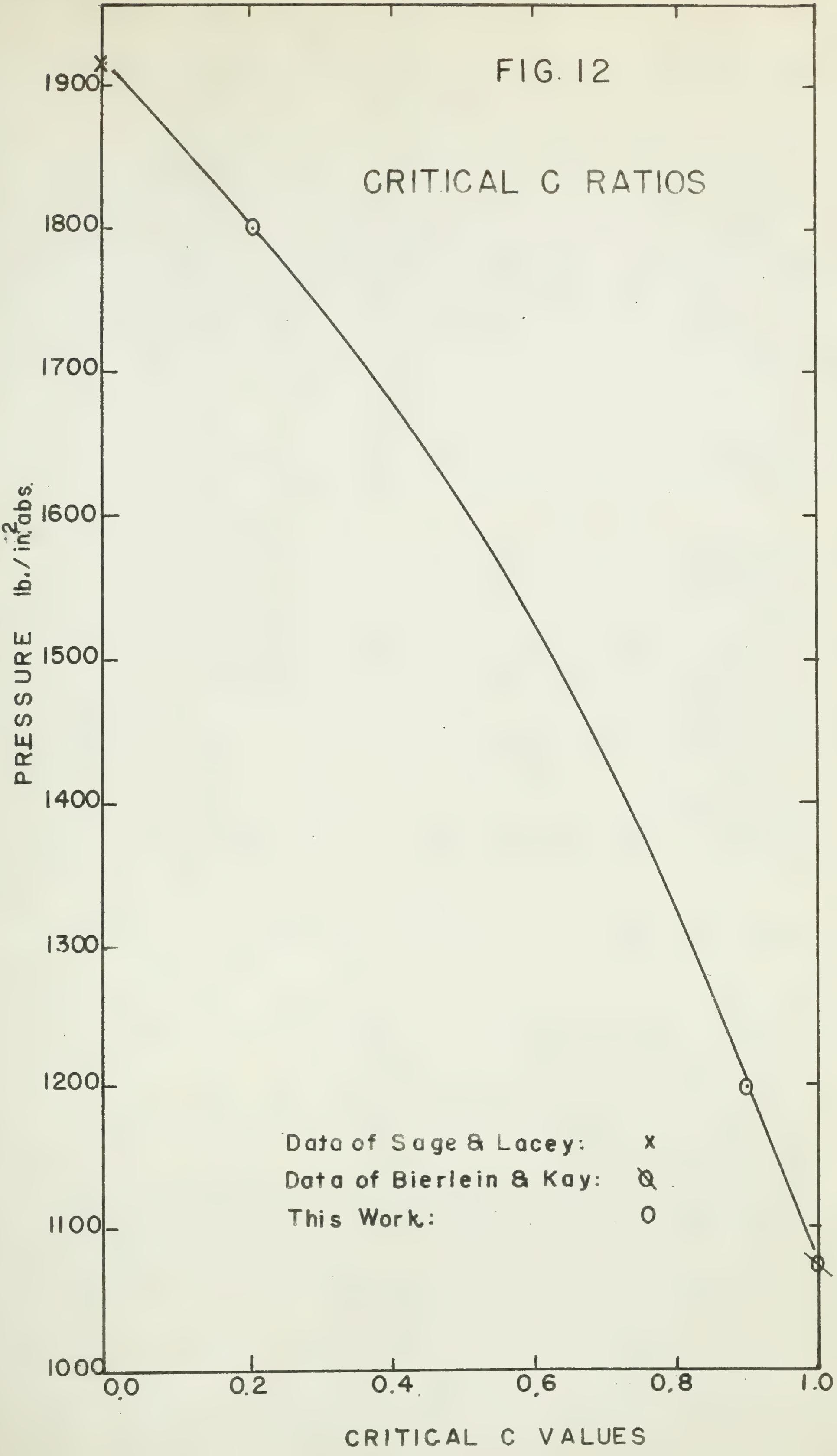

FIG. 12

CRITICAL C RATIOS

compositions referred to systems containing neither component.

At pressures below 600 lb/in.^{2}abs. the equilibrium curves for each component tend to merge indicating that the phase compositions are functions of pressure and temperature rather than of component concentrations. At higher pressures the curves all terminate at K values equal to unity at the critical pressure for each particular value of C. These pressures were determined by plotting the critical C values obtained from the published information on the binary pairs and the experimental ternary values against the critical pressures. The graph is shown by Fig.12.

The equilibrium values for the relatively non-volatile hydrogen sulfide which is primarily in the liquid phase, decrease from 1.0 at the vapor pressure of hydrogen sulfide through a series of values less than 1.0 returning to the limiting value of 1.0 at the critical pressure. Each C parameter curve passes through a minimum value of K. The proportion of hydrogen sulfide in the vapor phase never exceeds that in the liquid phase over the two phase region at 100 degrees F.

The variation of the equilibrium constants for methane and carbon dioxide are characteristic of volatile components, methane being the more volatile.

The constants decrease with increasing pressure to the limiting value of unity, indicating that the proportions of the components forced into the liquid phase increase with pressure. This behaviour is to be expected. The equilibrium constants for both components approach infinitely high values with the vapor pressure of hydrogen sulfide as an asymptote.

(b) Activity Coefficients

The system deviations from the idealized phase compositions as predicted by the combined Dalton's and Raoult's Laws were accounted in the calculation of activity coefficients. These values are recorded in Tables 6 and 7, Appendix I with the experimental K values from the equilibrium constant plots used in their calculations. The activity coefficients are plotted for each component as a function of system composition with pressure as a parameter. Figs.13, 14 and 15 indicate the activity coefficients for hydrogen sulfide-methane and carbon dioxide respectively.

The calculated activity coefficients for carbon dioxide and methane depended on the extrapolated vapor pressures for each. These activity coefficients are then not likely to be as significant as the values obtained for hydrogen sulfide. However, they still yield an estimate of the deviations from ideality.

The numerical magnitude of an activity coefficient is indicative of the effect the system deviation from ideality has upon the component, and the direction in which deviation is occurring.

Since the actual equilibrium constant is the ratio of the component proportion between the phases, then from the modified ideal solution law (6):

$$\text{Actual } K_i = \frac{\gamma_i P_i^*}{\pi} \quad \text{--- (10)}$$

Also from the ideal solution law (5), the theoretical equilibrium constant has the value given by:

$$\text{Theor. } K_i = \frac{P_i^*}{\pi} \quad \text{--- (11)}$$

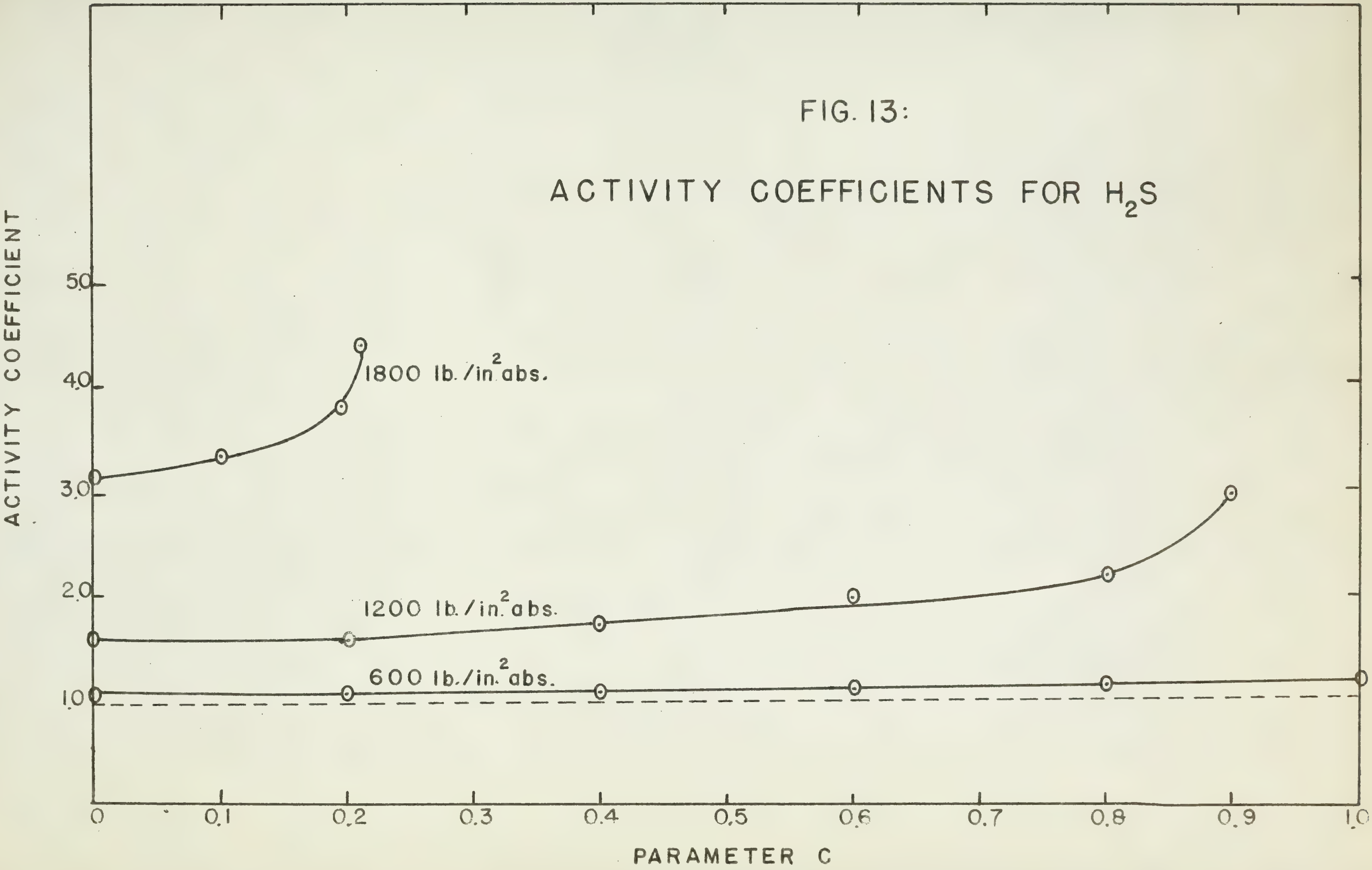

FIG. 13:

ACTIVITY COEFFICIENTS FOR H_2S

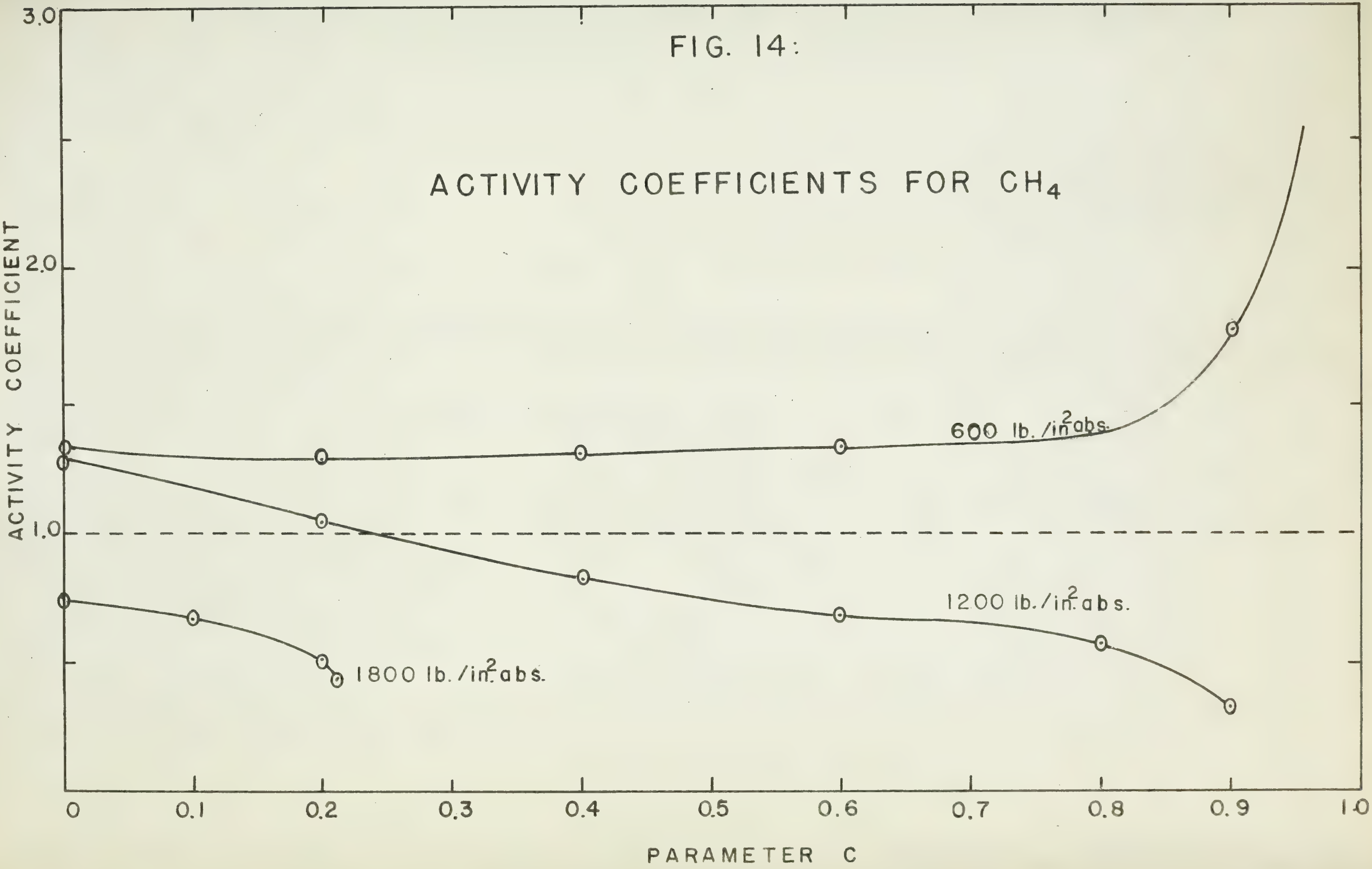

FIG. 14:

ACTIVITY COEFFICIENTS FOR CH_4

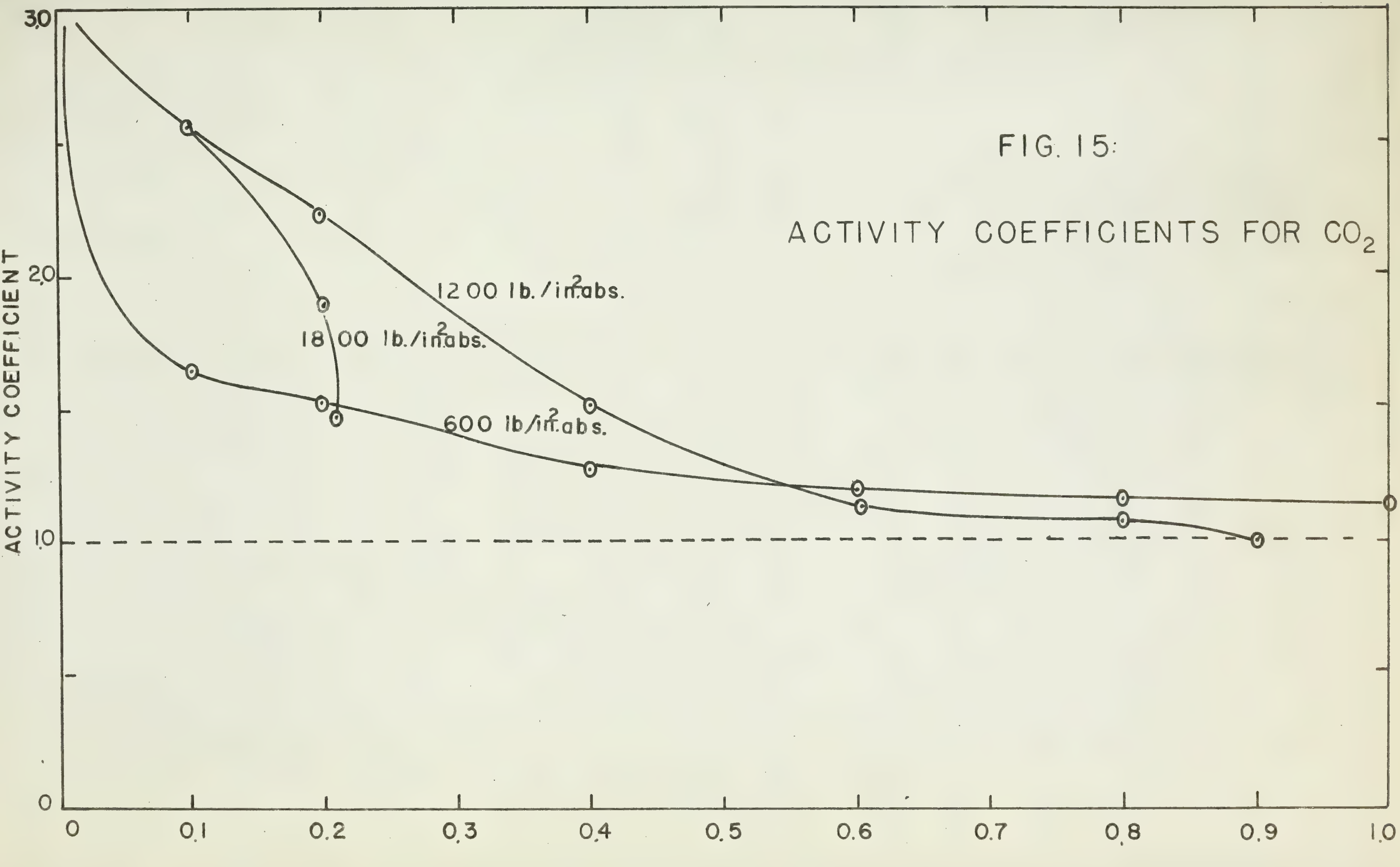
FIG. 15:

ACTIVITY COEFFICIENTS FOR CO_2

Hence dividing (10) by (11):

$$\gamma_i = \frac{\text{Actual } K_i}{\text{Theor. } K_i} \text{ --- (12)}$$

If the system is ideal, then the theoretical and actual experimental equilibrium constants are equivalent and the activity coefficient is unity. Values of the activity between one and zero signify the actual equilibrium constant is less than the theoretical. This indicates the component is distributed in higher amounts in the liquid phase and less in the vapor than predicted. Conversely, activity coefficients greater than unity are indicative of a shift in relative concentration to the vapor phase greater than the theoretical quantity.

The activity coefficients for hydrogen sulfide are independent of changing carbon dioxide-methane concentrations at 600 lb/in.^{2}abs. and are likely independent at all conditions below the pressures at which the ternary critical locus exists. The activity coefficient of hydrogen sulfide at 600 lb/in.^{2}abs. and 100 degrees F. is 1.46 which is the ratio of the system pressure to the vapor pressure. Therefore, the carbon dioxide and methane addition to hydrogen sulfide reduces its activity coefficient to an average value of 1.1. The hydrogen sulfide in the vapor phase is naturally reduced by the addition of volatile carbon dioxide and methane and the change in the activity coefficient represents this trend.

At 600 lb/in.^{2}abs. the activity coefficients of carbon dioxide and methane are also relatively independent of the overall system composition. However, as the proportion of carbon dioxide and methane tend to zero at the values of C equal to zero and unity respectively, the activity coefficients approach infinitely large values. This trend occurs only

at small proportions of these components in the ternary systems.

The activity coefficients of hydrogen sulfide increase with pressure and at the ternary critical pressures reach maximum values. Methane has an inverse behaviour, with coefficients decreasing with pressure and reaching minimum values at the critical compositions and pressures. Carbon dioxide has a behaviour characteristic of both the other components. It reaches minimum concentrations at the critical as does methane, but the activity coefficients increase with pressure for systems having a value of C less than 0.55 at least to 1200 $lb/in.^2$abs. At 1800 $lb/in.^2$abs. the trend is reversed, the coefficients being less than those at 1200 $lb/in.^2$abs.

The general conclusions resulting from the behaviour of the activity coefficients are that for each component they are relatively independent of system concentrations for pressures below the ternary critical locus. However, at pressures in the critical region and at compositions approaching the critical locus, non-volatile hydrogen sulfide tends to be displaced into the gas phase from the liquid phase by the more volatile methane and carbon dioxide and this trend is shown by the variation in the activity coefficients for each.

(c) Experimental Compressibility Factors

Experimental compressibility factors were calculated for the saturated vapor phases for most experimental runs at the equilibrium conditions. The values are listed in Table 8 and are plotted as functions of the compositions. The results were graphically smoothed in Fig.16. Some of the plotted data are widely scattered, primarily as the result of insufficiently accurate volumetric measurements on the vapor phase at the test conditions. Nevertheless, a definite trend is evident.

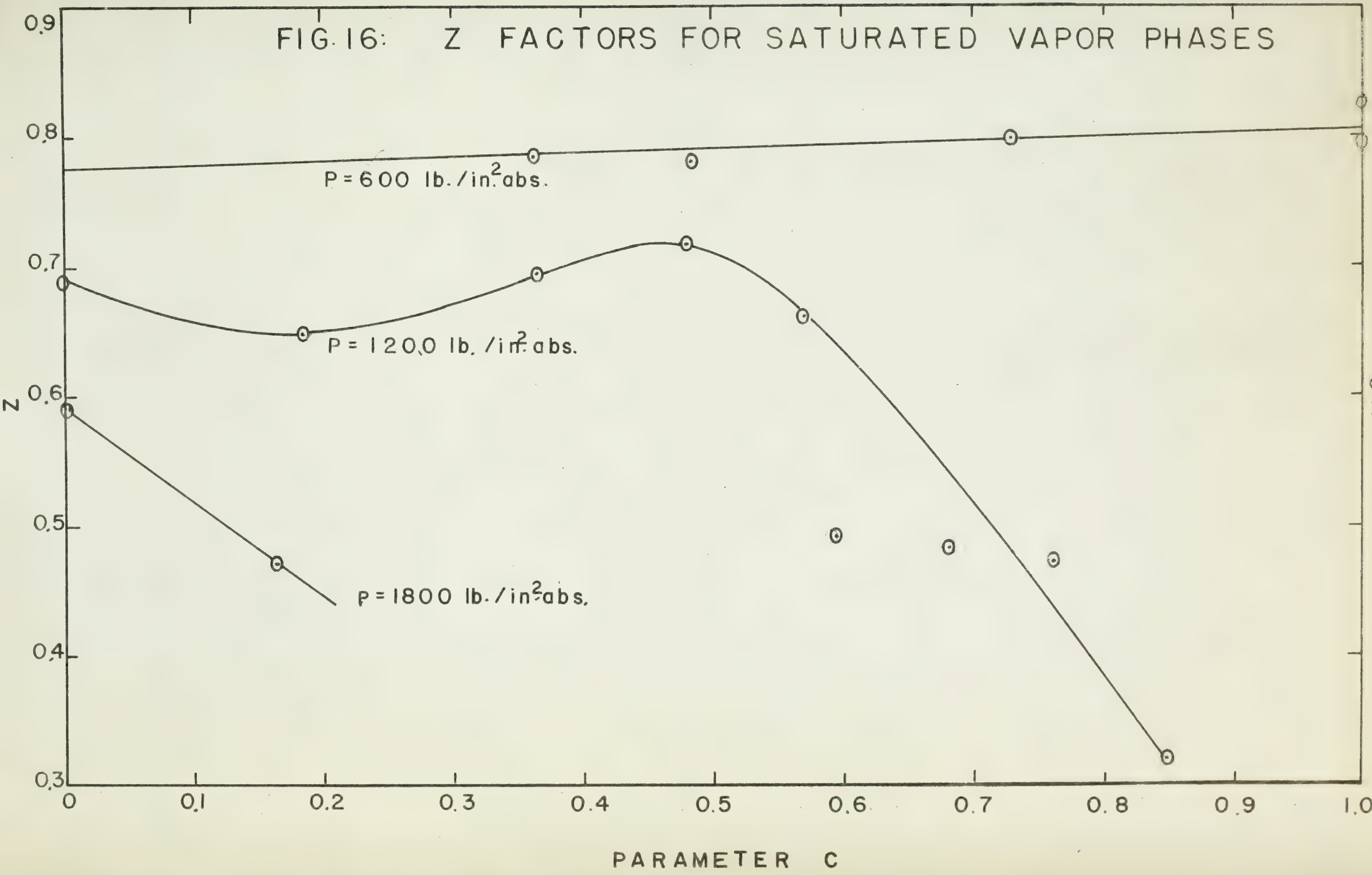

FIG. 16: Z FACTORS FOR SATURATED VAPOR PHASES

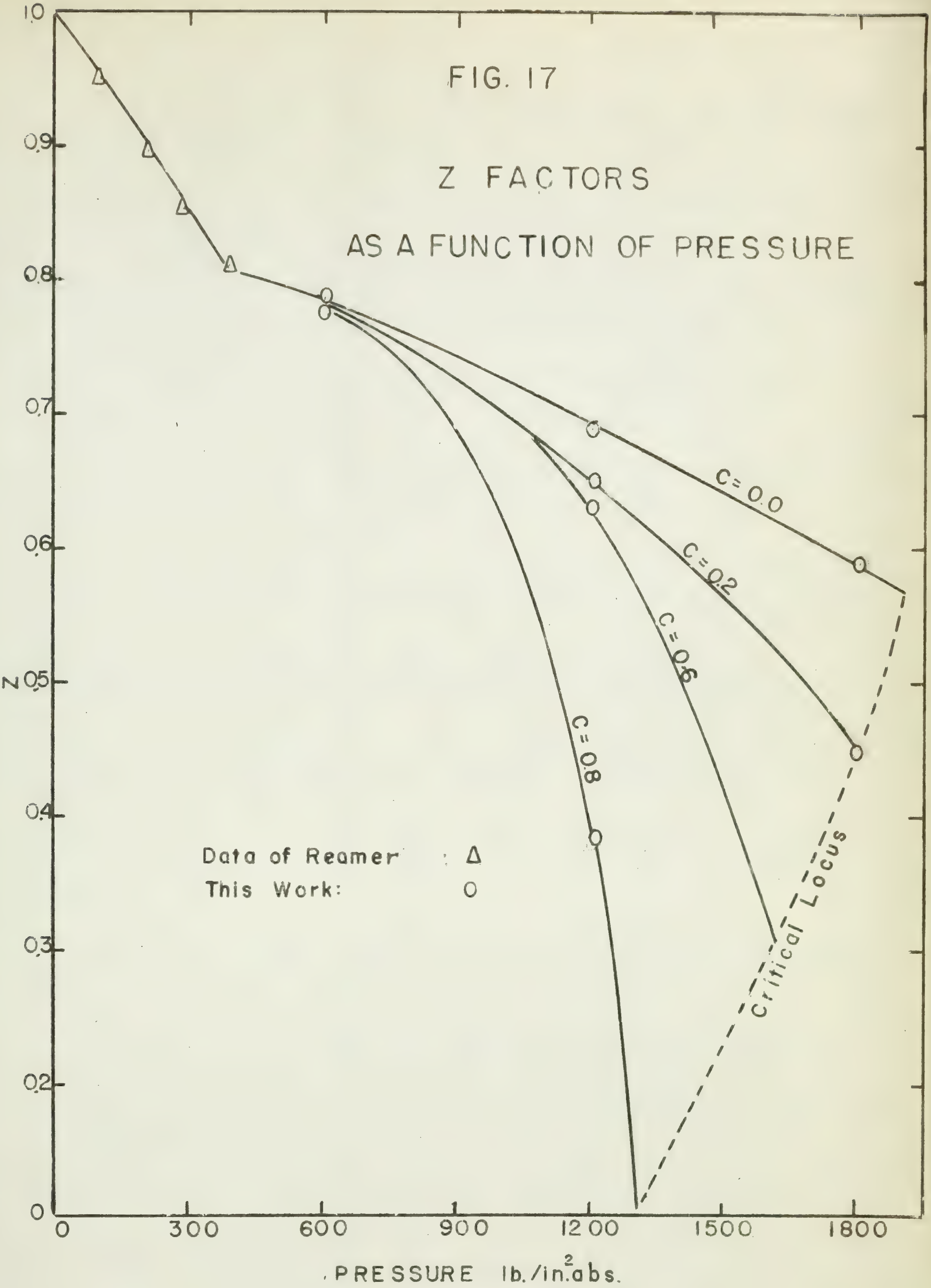

FIG. 17

Z FACTORS

AS A FUNCTION OF PRESSURE

As the composition of the vapor phase approaches the critical locus the phase becomes more incompressible since it is behaving more as a liquid than a gas. This change is reflected by the values of the compressibility factor becoming increasingly less than unity as the vapor phase becomes less ideal. Fig.16 indicates that at 600 lb/in.^{2}abs. the smoothed compressibility factors remain relatively constant as the system compositions change. However, for systems approaching the critical point and having a value of the composition parameter C higher than 0.5 at 1200 lb/in.^{2}abs., the compressibility factors show a significant deviation from unity. Values of C below 0.5 for 1200 lb/in.^{2}abs. the systems are sufficiently removed from the proximity of the critical locus that the compressibility factors remain relatively constant with composition. Similar behaviour is indicated at 1800 lb/in.^{2}abs. over the range of C values for the two-phase system.

Fig.17 shows a cross-plot of the smoothed data of Fig.16 versus pressure at regular values of C. This graph was plotted with a very few experimental points but nevertheless the increasing non-ideality of the gas phase with higher pressures is illustrated. At pressures below 900 lb/in.^{2}abs. the compressibility factors are apparently relatively independent of system compositions. The extrapolated values from 600 lb/in.^{2}abs. to the vapor pressure of hydrogen sulfide at 410 lb/in.^{2}abs. agree rather well with the published compressibility data of hydrogen sulfide (19) at pressures below its vapor pressure at 100 degrees F.

4. Prediction of Isobaric Phase Diagrams

The three equilibrium constant graphs were utilized to yield equilibrium constants at pressures of 900 and 1500 lb/in.^{2}abs. The constants were used in the derivation of isobaric phase diagrams at these pressures.

Since K_1, K_2 and K_3 represent the equilibrium constants for the components carbon dioxide-hydrogen sulfide and methane respectively, then:

$$K_1 = \frac{Y_1}{X_1} \quad \text{---} \ (13)$$

$$K_2 = \frac{Y_2}{X_2} \quad \text{---} \ (14)$$

$$K_3 = \frac{Y_3}{X_3} \quad \text{---} \ (15)$$

The ratio represented by the parameter C may be combined with equations (13), (14) and (15) to form further relations giving component mole fractions in terms of the known equilibrium ratios.

i.e.: $$X_1 = \frac{(1-K_2)CK_3}{CK_3(K_1-K_2)+K_1(K_3-K_2)(1-C)} \quad \text{---} \ (16)$$

and

$$X_3 = \frac{(1-C)K_1X_1}{CK_3} \quad \text{---} \ (17)$$

Equations (16) and (17) were combined with (13), (14) and (15) to determine the phase compositions at 900 and 1500 lb/in.^{2}abs. at even values of the parameter C. These calculated values are in Table 9, and the plots are shown in Figs.18 and 19 as well as in the composite pressure-composition diagram Fig.20.

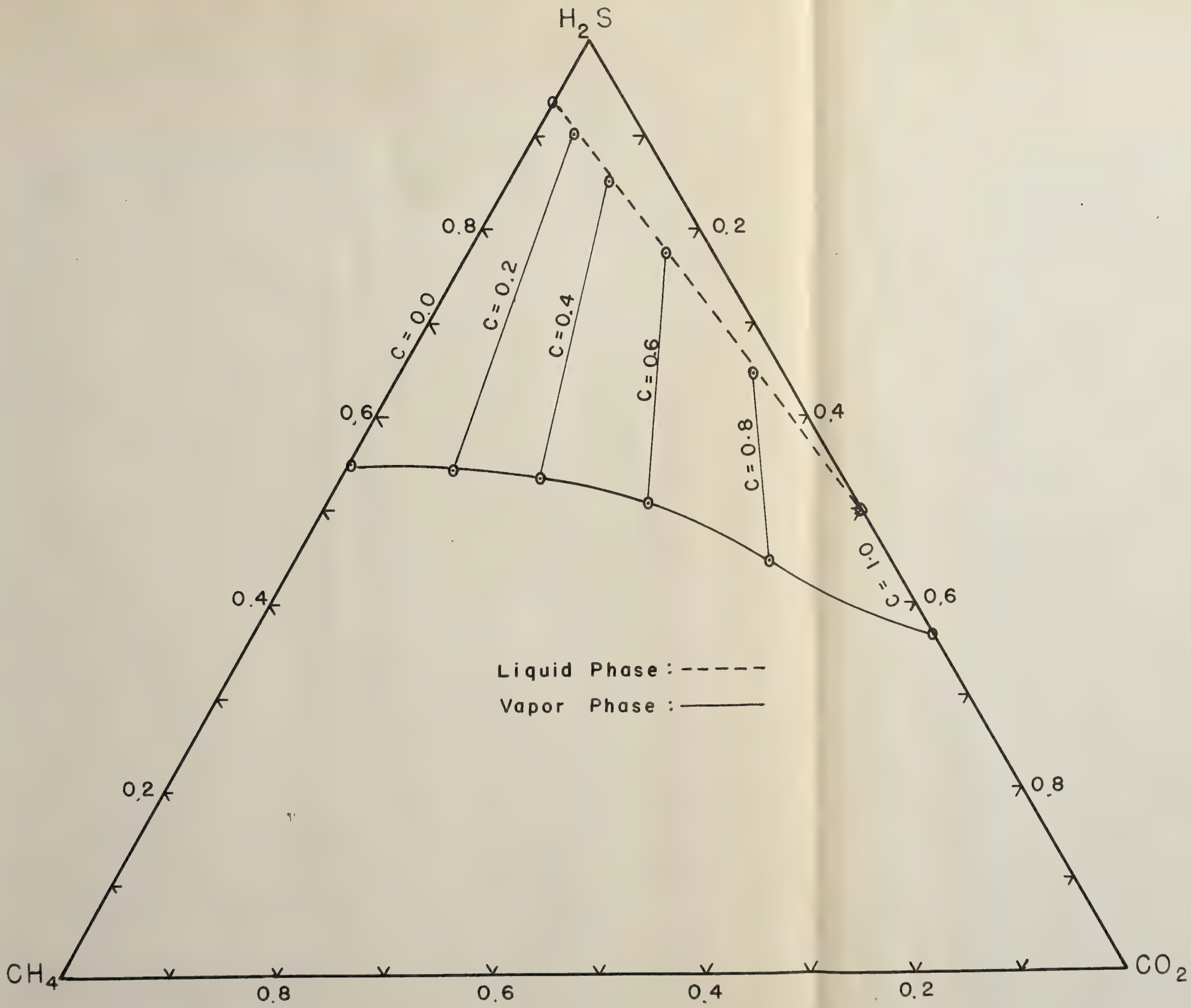

FIG. 18: PREDICTED MOLAR COMPOSITION DIAGRAM

T = 100°F. ; P = 900 lb./in.^{2} abs.

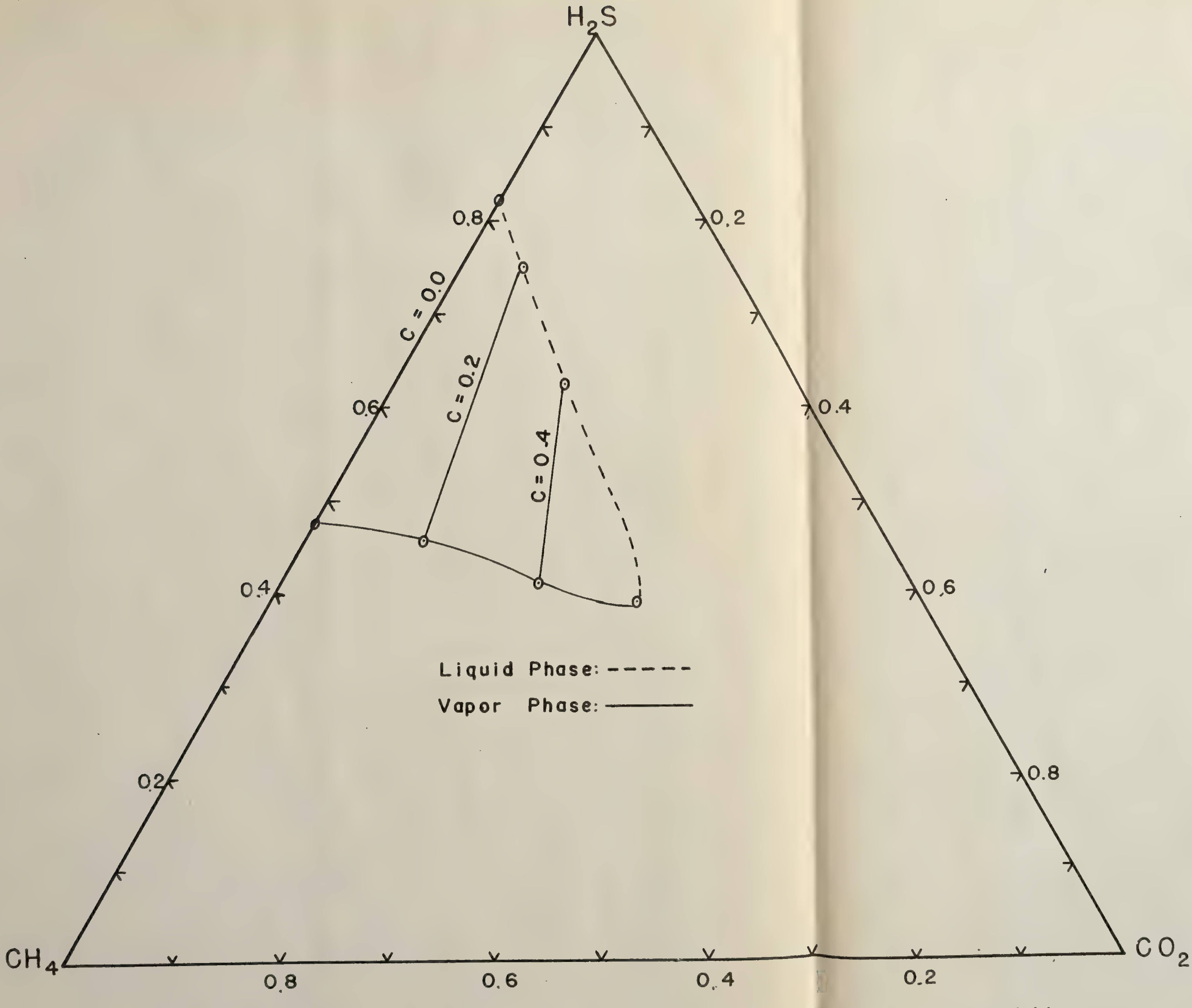

FIG. 19: PREDICTED MOLAR COMPOSITION DIAGRAM

T = 100 °F ; P = 1500 lb./in.^{2} abs.

This method of predicting phase diagrams is only as reliable as the equilibrium constants at the intermediate pressures. As the equilibrium constant curves were based on data for only three pressures, the graphical values of the equilibrium constants obtained for 900 and 1500 lb/in.^{2}abs. may be somewhat erroneous.

These equations were also utilized to determine the idealized isobaric composition diagrams for systems following the ideal solution law. With the ideal solution law the theoretical equilibrium constants can be expressed as the ratio of the vapor pressure of the component at the system temperature to the system pressure. Hence, the theoretical equilibrium constants may be determined providing the vapor pressure is known as a function of temperature.

The vapor pressure hydrogen sulfide from published data is 410 lb/in.^{2}abs. at 100 degrees F. The vapor pressures for carbon dioxide and methane were obtained by extrapolation of the known vapor pressures below their critical temperatures to 100 degrees F. The extrapolation was facilitated by using a plot of the natural logarithm of the vapor pressure versus the inverse of the absolute temperature. Such a plot is nearly linear. The fictitious extroplated values were found to be 4200 lb/in.^{2}abs. methane and 1220 lb/in.^{2}abs. carbon dioxide.

The predicted values reported in Table 10 for the liquid and gas phases are shown on the 600, 1200 and 1800 lb/in.^{2}abs. isobaric phase composition diagrams, Figs.6, 7 and 8, as a comparison with the actual values. The phase boundary surfaces for ideal solutions are flat and this behaviour is fairly well followed by the actual composition diagrams for 600 and 1200 lb/in.^{2}abs. The system at 600 lb/in.^{2}abs.

indicates fairly ideal behaviour, but at pressures above the critical for the hydrogen sulfide-carbon dioxide system a far greater deviation occurs.

The ideal diagrams being based on the extrapolated vapor pressures for carbon dioxide and methane, indicate that the hydrogen sulfide-carbon dioxide binary system exists without a critical point and the methane-carbon dioxide binary systems exist at 100 degrees F. at pressures within the experimental range. Hence the idealized diagram at 1800 lb/in.^{2}abs. bears no apparent relation to the actual system. However, the similarity between the two is unmistakable at lower pressures. The liquid phase as determined experimentally and the idealized liquid phase are more closely approximate in composition than are the actual gas and ideal gas phases. Therefore, the liquid phase is nearer ideality than the gas phase.

5. The Behaviour of the Three Component System at 100 Degrees F.

The complete ternary phase diagram for the system is represented by Fig.20. The outline of the heterogeneous region has been indicated to some extent with the three isobaric test sections through the heterogeneous region at 600, 1200 and 1800 lb/in.^{2}abs., as well as the two predicted sections at 900 and 1500 lb/in.^{2}abs. The two binary pressure-composition diagrams representing the termination of the three component heterogeneous region are also shown.

Each isobaric phase diagram has the positions of the tie-lines indicated at regular values of the parameter C. The line joining the tie-lines at 0.2 C for the five pressures represents the phase boundary surfaces for similar systems at all intermediate pressures. The portion

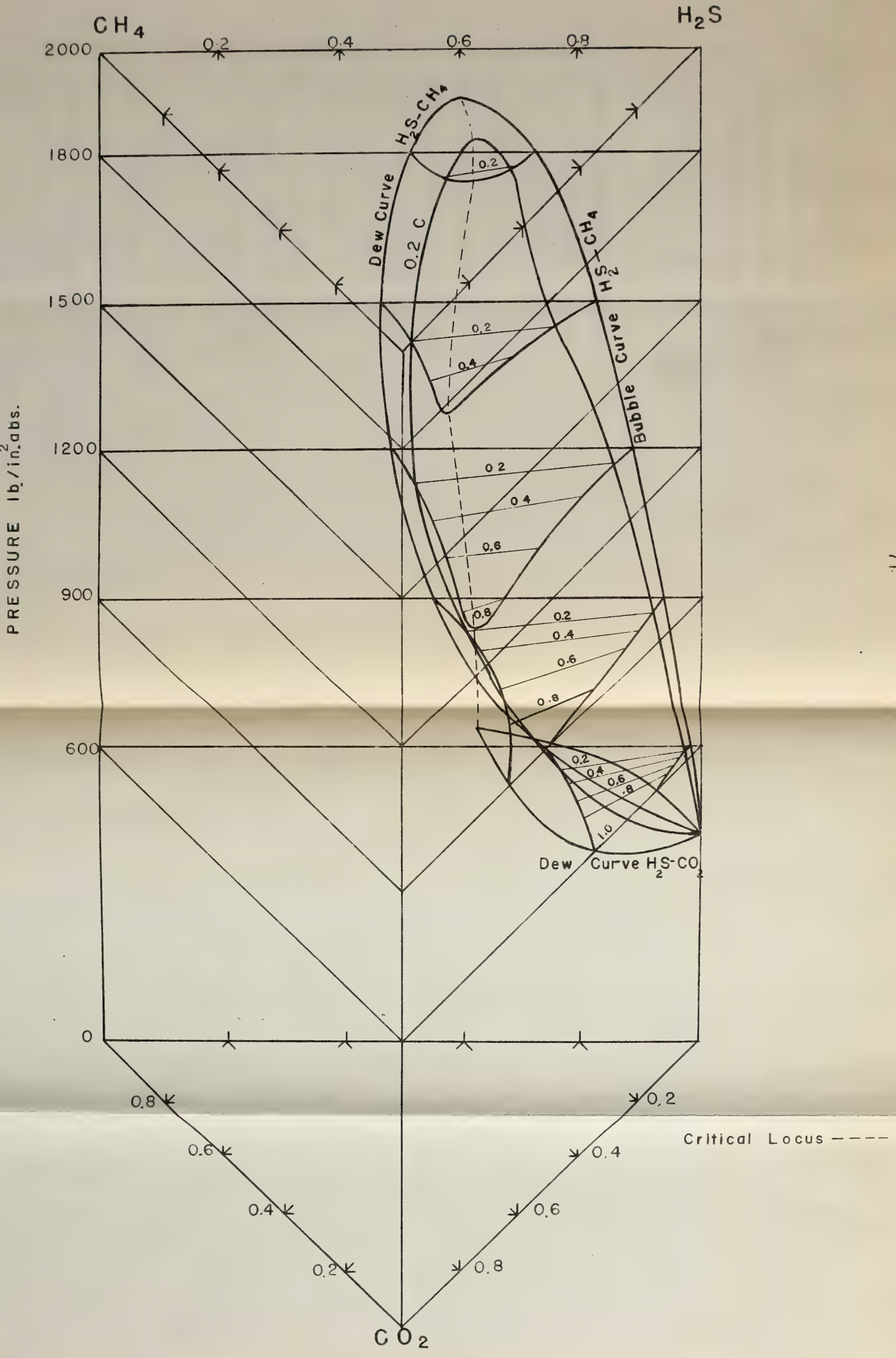

FIG. 20: PHASE DIAGRAM FOR THE TERNARY SYSTEM
$T = 100°F.$

of the line representing the vapor phase and that representing the liquid phase intersect at the critical pressure of the system corresponding to 0.2 C. This pressure from Fig.12 is 1810 lb/in.^{2}abs. Similar lines could be shown for the remaining C values but have been omitted from the diagram to improve the clarity. These lines on the liquid and vapor boundary surfaces would terminate at 410 lb/in.^{2}abs. at the hydrogen sulfide vertex of the phase diagram.

The nature of the heterogeneous region is dependent to a large extent upon the characteristics of the components at 100 degrees F. The methane in the binary methane-hydrogen sulfide system is much more volatile than hydrogen sulfide so it enters the liquid phase only in relatively small amounts. The proportion in the liquid phase increases only slightly with pressure as is shown by the binary pressure-composition curves of Fig.20, and the hydrogen sulfide-methane isothermal diagram Fig.3. Due to the widespread difference in volatilities between the two components, the vapor phases are considerably richer in methane than the liquid. Although the critical pressure of hydrogen sulfide is 1435 lb/in.^{2}abs.(11), and that for methane is 690 lb/in.^{2}abs.(14); the critical pressures of certain intermediate systems pass through maximum values higher than either component. This accounts for the relatively high critical pressure for the system at 100 degrees F.

The hydrogen-sulfide-carbon dioxide pair represented on the three component phase diagram or by Fig.2., exhibits somewhat similar behaviour. However, as the system temperature does not greatly exceed the critical temperature of carbon dioxide, the binary critical point is much richer in this volatile component than was the corresponding critical point in the hydrogen sulfide-methane system. Since carbon dioxide is between hydrogen sulfide and methane in volatility, the composition

differences between the liquid and gas phases of the carbon dioxide-hydrogen sulfide systems are not as great as for corresponding methane-hydrogen sulfide systems. The critical pressure of carbon dioxide at 87.6 degrees F. is 1060 lb/in.^{2}abs.(4), and the critical pressures of all carbon dioxide-hydrogen sulfide mixtures are intermediate between this pressure and the critical pressure of hydrogen sulfide. Hence the critical pressure for this system is much lower than the binary critical pressure of hydrogen sulfide-methane.

The known behaviour of the two binary isothermal phase diagrams and the five isobaric phase diagrams for the ternary systems serve to define the three component heterogeneous region at 100 degrees F. At pressures below 410 lb/in.^{2}abs. no liquefaction can occur for any three component system. At 410 lb/in.^{2}abs. the initial vapor to liquid transformation occurs but only for a system composed entirely of hydrogen sulfide. However, at successively higher pressures co-existing three component liquid-vapor phases are possible for compositions in the heterogeneous region. The initial systems must be very high in hydrogen sulfide. However, as pressures increase the heterogeneous region shifts towards the carbon dioxide and methane vertices of the phase diagram following the behaviour of the two binary phase diagrams.

Between 410 lb/in.^{2}abs. and 1075 lb/in.^{2}abs. the heterogeneous region extends between the hydrogen sulfide-methane and hydrogen sulfide-carbon dioxide phase boundary curves. The proportion of hydrogen sulfide in the co-existing phases in the ternary region becomes uniformly less from the hydrogen sulfide-methane boundary to the hydrogen sulfide-carbon dioxide boundary as indicated by the ternary composition sections at 600 and 900 lb/in.^{2}abs. At 700 lb/in.^{2}abs. the two phases

for the hydrogen sulfide-carbon dioxide system are most dissimilar with respect to composition. From this pressure to 1075 lb/in.^{2}abs. the liquid and gas phases for this system approach in composition while the proportion of carbon dioxide in each increases at 1075 lb/in.^{2}abs. the two phases reach the same composition at the binary critical point of 0.73 mole fraction carbon dioxide. Therefore, while ternary systems in equilibrium near the hydrogen sulfide-carbon dioxide axis shift to higher proportions of carbon dioxide with increasing pressure; the concentration gradient between the phases steadily decreases from 700 lb/in.^{2}abs. At 1075 lb/in.^{2}abs. the ternary liquid and vapor phase surfaces meet at the binary hydrogen sulfide-carbon dioxide critical locus.

Above 1075 lb/in.^{2}abs. the heterogeneous region decreases in magnitude retreating to the methane-hydrogen sulfide boundary where it disappears at 1910 lb/in.^{2}abs. and at 0.40 mole fraction methane. The phase boundary surfaces over this pressure range meet at the locus of the ternary critical systems. At pressures above 1600 lb/in.^{2}abs. the composition spread between the phase boundary surfaces also decreases as a result of the approach of the dew point and bubble point curves for the methane-hydrogen sulfide phase diagram near the binary critical pressure.

In general, the heterogeneous region at 100 degrees F. is limited to systems rich in hydrogen sulfide since it originates at the hydrogen sulfide vertex and due to the widespread differences between the critical temperatures of the components, it never approaches the methane or carbon dioxide vertices.

VI CONCLUSIONS

1. Experimental Data

The heterogeneous region for the hydrogen sulfide-carbon dioxide-methane system at 100 degrees F. was defined by the determination of three isobaric ternary phase diagrams. The following general conclusions apply to the phase behaviour of the system:

1. The system forms co-existing, liquid-vapor phases from the vapor pressure of hydrogen sulfide at 410 lb/in.^{2}abs. to the critical pressure of the binary hydrogen sulfide-methane system at 1910 lb/in.^{2}abs. The compositions of the co-existing phases are limited to systems rich in hydrogen sulfide since at 100 degrees F. this is the only component which exists as a liquid under its vapor pressure.

2. The liquid phase is relatively more ideal at all pressures and compositions than the vapor phase. This is indicated by comparison of the idealized isobaric phase diagrams with the actual. There is no tendency toward the formation of ternary azeotropic mixtures although the isobaric vapor phase compositions do show a slight curvature toward the liquid phase compositions.

3. A locus of ternary critical systems exists over a pressure and composition range varying from the hydrogen sulfide-carbon dioxide binary pair at 0.27 mole fraction hydrogen sulfide and 1075 lb/in.^{2}abs. to 0.60 mole fraction hydrogen sulfide and 1910 lb/in.^{2}abs. for the hydrogen sulfide-methane system. There is no evidence to indicate that the ternary critical locus exists at a unique point having a pressure higher than that of the hydrogen sulfide-methane system critical point.

4. The combined deviation of the liquid and gas phases from ideality was expressed by the calculation of activity coefficients

for each component with the experimental data. The ideality of the saturated vapor phases at the test conditions was also determined by means of compressibility factors. In general, these data indicate that the ideality is dependent upon pressure at system pressures below the ternary critical range but is dependent upon both pressures and system compositions in the ternary critical range.

5. The experimental phase composition data were used to determine equilibrium constants for each component. This is the most practical means for the expression of the ternary system equilibrium data. The equilibrium constants indicate that at pressures below the ternary critical range, the vapor to liquid proportion of each component is relatively independent of the overall system composition but depends rather on the system pressure. Within the ternary critical range however, the system compositions influence the equilibrium ratios.

The hydrogen sulfide is primarily in the liquid phase and its non-volatility is reflected in equilibrium constants less than or equal to unity. The equilibrium constants for hydrogen sulfide are unity both at its vapor pressure and at the critical states. Methane, and carbon dioxide are more volatile having equilibrium constants greater than or equal to unity. The equilibrium constants for carbon dioxide and methane are unity only for the particular system compositions corresponding to the critical points.

2. Validity of Experimental Results

The merit of experimental phase equilibrium work is directly related to the precision in which the system variables pressure,

temperature, volume and composition are controlled and measured.

During the test runs, pressures were determined to ± 1 lb/in.^{2} below 1,000 lb/in.^{2} and ± 3 lb/in.^{2} above. While the desired equilibrium pressures were maintained within these limits during the achievement of equilibrium, significant pressure changes could occur during the sampling operation. Unless isobaric conditions were maintained during the vapor phase sampling and phase separation operations, the equilibrium state conditions would be destroyed and the resulting samples secured not representative of the true equilibrium. However, it was possible while sampling to maintain pressures within ± 2 lb/in.^{2} at the 600 lb/in.^{2}abs series and ± 5 lb/in.^{2} at the higher pressures. Since the gas phase was quickly secured there was little chance for a significant equilibrium change to occur during the sampling.

However, the noticeable deviation of some liquid analyses particularly near the region of the ternary critical points, could be partially attributable to the loss in equilibrium during the phase separation operation. This was a lengthy operation in contrast to the vapor phase sampling so there was an opportunity for phase changes to occur.

The temperature control of the system was adequate since the temperature of the cell could generally be maintained within ± 0.1 degrees of 100 degrees F. during runs. Although the air bath temperature occasionally varied by ± 0.5 degrees F., the heat input was corrected before the cell temperature was significantly affected.

The accuracy of the volumetric measurements was limited by the precision of the cathotometer readings and the use of the calibration charts. It is felt that the volumes were obtained to the nearest 0.1 cc. This was sufficiently accurate for the measurement of the components but not for the calculation of the liquid phase analysis.

It is estimated that the analysis obtained by the Orsat and Tutweiler could have been in error by a maximum of ± 1%.

3. Proposed Work

The behaviour of the three component system may be investigated at other temperature levels. The phase equilibria at higher temperatures than 100 degrees F. could be determined since the critical temperature for hydrogen sulfide is 212 degrees F., and ternary systems will form two phases to this temperature. It is expected that at higher temperatures the heterogeneous region would exist over a narrower range of carbon dioxide and methane compositions as well as pressures, due to the increasingly widespread difference between the system temperatures and the critical temperatures for methane and carbon dioxide. The initial liquefaction in the system would occur at higher pressures corresponding to the increase in vapor pressure of hydrogen sulfide with temperature. No further modification of the existing apparatus is required for higher temperature runs, since the present heating system is adequate.

At temperatures below 100 degrees F., the heterogeneous region would exist closer to the carbon dioxide-methane axis as the critical temperature of carbon dioxide at 87.6 degrees F. is approached. The initial liquefaction pressure of the system would be lower,

corresponding to the decrease in vapor pressure of hydrogen sulfide.

At 87 degrees F. and at lower temperatures, the binary critical for the hydrogen sulfide-carbon dioxide systems is no longer present and the carbon dioxide-methane systems form two phases for mixtures rich in carbon dioxide. Therefore, below the critical temperature of carbon dioxide the heterogeneous three component system can exist over a composition range extending to the carbon dioxide-methane boundary. In general, the co-existing liquid and gas phases below 100 degrees F. will be richer in carbon dioxide and methane than those above 100 degrees F.

The lowest temperature at which the present equipment will operate is -38 degrees F., which represents the freezing point of the mercury used as the confining media in the equilibrium cell.

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APPENDICES:

I - TABULATED DATA

II - EXPERIMENTAL PROCEDURE

III - SAMPLE CALCULATIONS

TABLE NO. 1

Summary of Phase Composition Data For Series I Runs
At T = 100 Deg. F. P = 600 lb/in.^{2} abs.

Run No.	Total System Analysis*			Vapor Phase Analysis			Liquid Phase Analysis			Calculated Liquid Phase		
	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4
I - I	0.796	0.204	0.0	0.608	0.392	0.0	0.840	0.160	0.0	0.840	0.160	0.0
II- I	0.792	0.143	0.065	0.660	0.222	0.118	0.810	0.170	.020	0.921	0.073	0.005
III-I	0.776	0.152	0.072	0.667	0.206	0.127	0.905	0.069	0.026			#
IV- I	0.882	0.053	0.060	0.684	0.115	0.201	0.937	0.044	0.019	0.934	0.043	0.023
V - I	0.790	0.159	0.051	0.644	0.259	0.097	0.891	0.101	0.008	0.899	0.091	0.011
VI- Ia	0.804	0.196	0.0	0.630	0.370	0.010				0.815	0.185	0.0
VI- Ib	0.745	0.180	0.025	0.630	0.317	0.053	0.870	0.122	0.008			#
VII-I	0.888	0.0	0.122	0.710	0.0	0.290	0.967	0.0	0.033			
VIII-I	0.855	0.039	0.106	0.690	0.066	0.244	0.955	0.029	0.016			

* All Compositions are in Terms of Mole Fractions

# Calculated Liquid Compositions are not Reported Due to Negative Values

TABLE NO. 2

Summary of Phase Composition Data For Series II Runs
At T = 100 Deg. F. P = 1200 lb/in.^{2}abs.

Run No.	Total System Analysis			Vapor Phase Analysis			Liquid Phase Analysis			Calculated Liquid Phase		
	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4
I - II	0.775	0.0	0.225	0.490	0.00	0.510				0.786	0.0	0.214
II- II	0.732	0.052	0.216	0.470	0.095	0.435	0.843	0.042	0.115	0.852	0.032	0.116
III-II	0.666	0.148	0.185	0.945	0.201	0.354	0.747	0.137	0.116	0.784	0.095	0.120
IV- II	0.637	0.216	0.147	0.918	0.278	0.304	0.683	0.213	0.104			#
V - II	0.546	0.306	0.147	0.411	0.332	0.257	0.615	0.284	0.101	0.645	0.284	0.071
VI- II	0.532	0.323	0.144	0.407	0.347	0.246	0.598	0.305	0.097	0.604	0.311	0.087
VII-II	0.456	0.390	0.155	0.368	0.422	0.210	0.552	0.376	0.082	0.538	0.390	0.071
VIII-II	0.391	0.478	0.131	0.348	0.498	0.155	0.416	0.458	0.066	0.473	0.460	0.068
IX- II	0.394	0.525	0.082	0.314	0.565	0.121	0.422	0.520	0.058			
X - II	0.342	0.578	0.081	0.316	0.579	0.105	0.372	0.763	0.065	0.368	0.576	0.056
XI- II	0.314	0.616	0.070	Critical System Composition For 1200 lb/in.^{2}abs.								

TABLE NO. 3

Summary of Phase Composition Data For Series III Runs
At T = 100 Deg. F. P = 1800 lb/in.^{2}abs.

Run No.	Total System Analysis			Vapor Phase Analysis			Liquid- Phase Analysis			Calculated Liquid Phase		
	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4
I - III	0.626	0.0	0.374	0.522	0.0	0.478	0.740	0.0	0.260	0.720	0.0	0.280
II- III	0.551	0.084	0.364	System at Vapor Locus Exhibiting Retrograde Behaviour								
III-III	0.590	0.059	0.357	0.530	0.047	0.423	0.706	0.036	0.258	0.790	0.052	0.150
IV-IIIa	0.602	0.090	0.308	System Exhibited Critical Color Phenomena at 1790 lb/in.^{2}abs.								
IV-IIIb	0.577	0.087	0.336	System at Vapor Locus Exhibiting Retrograde Behaviour								
V - III	0.611	0.083	0.306	Critical System Composition For 1800 lb/in.^{2}abs.								
VI- III*	0.611	0.059	0.329	0.520	0.079	0.401	0.655	0.050	0.285	0.698	0.041	0.262

* Repeat of Run III - III

TABLE NO. 4

Experimental Equilibrium Constants At Regular Values

of The Parameter C For 600 lb/in.^{2}abs.

Value of C	Composition of Vapor Phase			Composition of Liquid Phase			Equilibrium Constant		
	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4
0.0	0.710	0.0	0.290	0.966	0.0	0.034	0.735	-	8.55
0.2	0.690	0.063	0.247	0.952	0.020	0.028	0.725	3.14	8.96
0.4	0.680	0.128	0.192	0.930	0.050	0.020	0.731	2.56	9.60
0.6	0.668	0.200	0.132	0.896	0.090	0.014	0.745	2.22	9.43
0.8	0.640	0.288	0.072	0.876	0.116	0.008	0.730	2.48	9.00
1.0	0.610	0.390	0.0	0.840	0.160	0.0	0.726	2.44	-

TABLE NO. 5

Experimental Equilibrium Constants at Regular Values

of the

Parameter C for 1200 lb/in.^{2}abs. and 1800 lb/in.^{2}abs.

Value of C	Composition of Vapor Phase			Composition of Liquid Phase			Equilibrium Constant		
	H_2S	CO_2	CH4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4
				For 1200 lb/in.^{2}abs.					
0.0	0.490	0.0	0.510	0.895	0.0	0.105	0.548	-	4.85
0.2	0.468	0.105	0.427	0.842	0.046	0.112	0.556	2.28	3.81
0.4	0.439	0.225	0.336	0.735	0.148	0.117	0.597	1.52	2.87
0.6	0.402	0.360	0.235	0.585	0.315	0.100	0.688	1.14	2.38
0.8	0.325	0.540	0.135	0.435	0.500	0.065	0.747	1.08	2.08
				For 1800 lb/in.^{2}abs.					
0.0	0.519	0.0	0.481	0.720	0.0	0.280	0.721	-	1.72
0.2	0.550	0.090	0.360	0.630	0.070	0.300	0.874	1.29	1.20

TABLE NO. 6

Activity Coefficients At Regular Values of the Parameter C at 600 lb/in.^{2}abs.

Value of C	Experimental K Values			Theoretical K Values			Activity Coefficients		
	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4
0.0	0.735	-	8.8	0.685	2.04	7.00	1.07	-	1.26
0.1	0.74	3.26	8.9	0.685	2.04	7.00	1.08	1.61	1.27
0.2	0.74	3.14	8.9	0.685	2.04	7.00	1.08	1.54	1.27
0.4	0.74	2.58	9.1	0.685	2.04	7.00	1.08	1.27	1.30
0.6	0.745	2.42	9.4	0.685	2.04	7.00	1.09	1.19	1.34
0.8	0.76	2.34	9.4	0.685	2.04	7.00	1.11	1.15	1.34
0.9	0.76	2.32	12.7	0.685	2.04	7.00	1.11	1.14	1.82
1.0	0.77	2.30	-	0.685	2.04	7.00	1.12	1.13	-

TABLE NO. 7

Activity Coefficients At Regular Values
of the
Parameter C at 1200 and 1800 lb/in.^{2}abs.

For 1200 lb/in.^{2}abs.

Value of C	Experimental K Values			Theoretical K Values			Activity Coefficients		
	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4
0.0	0.54	-	4.85	0.342	1.02	3.50	1.58	-	1.39
0.1	0.55	2.58	4.32	0.342	1.02	3.50	1.61	2.52	1.23
0.2	0.55	2.29	3.83	0.342	1.02	3.50	1.61	2.25	1.10
0.4	0.60	1.54	2.88	0.342	1.02	3.50	1.75	1.51	0.83
0.6	0.69	1.16	2.38	0.342	1.02	3.50	2.02	1.14	0.68
0.8	0.73	1.08	2.08	0.342	1.02	3.50	2.13	1.06	0.60
0.9 (Critical)	1.00	1.00	1.00	0.342	1.02	3.50	2.92	0.98	0.29

For 1800 lb/in.^{2}abs.

Value of C	Experimental K Values			Theoretical K Values			Activity Coefficients		
	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4
0.0	0.72	-	1.72	0.228	0.666	2.34	3.16	-	0.74
0.1	0.75	1.72	1.55	0.228	0.666	2.34	3.30	2.56	0.67
0.2	0.87	1.28	1.19	0.228	0.666	2.34	3.82	1.90	0.51

TABLE NO. 80

EXPERIMENTAL COMPRESSIBILITY FACTORS

FOR

SATURATED VAPOR PHASES AT 100 DEG. F.

P = 600 lb/in.^{2}abs.				P = - 1200 lb/in.^{2}abs.				P = 1800 lb/in.^{2}abs.			
C	V*	n^+	Z_m	C	V	n	Z_m	C	V	n	Z_m
0.0	18.0	0.0294	0.980	0.0	6.2	0.0288	0.69	0.0	6.9	0.0562	0.59
0.220	21.8	0.0351	0.994	0.187	6.6	0.0325	0.65	0.166	5.5	0.0584	0.45
0.365	10.5	0.0215	0.782	0.363	7.5	0.0346	0.695				
0.475	30.2	0.0619	0.781	0.480	4.7	0.0210	0.715				
0.73	21.1	0.0422	0.800	0.570	7.8	0.0379	0.66				
1.00	8.8	0.0177	0.795	0.590	6.7	0.0438	0.49				
1.00	10.75	0.0209	0.823	0.680	14.65	0.0967	0.485				
				0.760	19.8	0.1348	0.47				
				0.826	11.1	0.0759	0.47				
				0.850	10.4	0.1038	0.32				

* Volume of Saturated Vapor Phase - cc.

+ Gram-moles of Saturated Vapor Phase

TABLE NO. 9

Predicted Phase Compositions at 900 and 1500 lb/in.^{2}abs.

	For 900 lb/in.^{2}abs.						For 1500 lb/in.^{2}abs.					
C Values	Liquid Phase Analysis			Vapor Phase Analysis			Liquid Phase Analysis			Vapor Phase Analysis		
	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4
0.0	0.93	0.0	0.07	0.55	0.0	0.45	0.82	0.0	0.18	0.475	0.0	0.525
0.2	0.905	0.035	0.06	0.55	0.10	0.35	0.75	0.06	0.19	0.45	0.11	0.44
0.4	0.845	0.10	0.055	0.535	0.185	0.28	0.62	0.16	0.22	0.41	0.24	0.35
0.6	0.775	0.185	0.04	0.51	0.30	0.19						
0.8	0.65	0.325	0.025	0.45	0.44	0.11						
1.0	0.50	0.50	0.0	0.375	0.625	0.0						

Estimated Critical Composition for 1500 lb/in.^{2}abs.

$H_2S = 0.39$

$CO_2 - 0.34$

$CH_4 - 0.27$

TABLE NO. 10

PHASE COMPOSITIONS FOR IDEAL SYSTEMS AT 600, 1200 AND 1800 lb/in.^{2}abs.

	600 lb/in.^{2}abs.						1200 lb/in.^{2}abs.						1800 lb/in.^{2}abs.					
	Liquid Phase			Vapor Phase			Liquid Phase			Vapor Phase			Liquid Phase			Vapor Phase		
C	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4	H_2S	CO_2	CH_4
0.0	0.950	0.0	0.050	0.650	0.0	0.350	0.791	0.0	0.209	0.270	0.0	0.730	0.630	0.0	0.370	0.144	0.0	0.856
0.2	0.922	0.036	0.042	0.632	0.074	0.294	0.673	0.151	0.176	0.230	0.154	0.616	0.425	0.266	0.309	0.100	0.180	0.720
0.4	0.889	0.077	0.034	0.608	0.157	0.235	0.553	0.318	0.139	0.190	0.324	0.486	0.190	0.564	0.246	0.044	0.382	0.574
0.6	0.853	0.123	0.024	0.582	0.251	0.167	0.392	0.509	0.099	0.134	0.520	0.436						
0.8	0.812	0.175	0.127	0.554	0.357	0.089	0.225	0.722	0.053	0.080	0.736	0.184						
1.0	0.766	0.234	0.0	0.552	0.478	0.0	0.030	0.970	0.0	0.110	0.989	0.0						

TABLE NO. 11

TEST DATA FOR RUN II - II

Equilibrium Conditions: T = 100° F.

P = 1200° F.

PART I: Phase Conditions for Components Added to Equilibrium Cell

(a) Component Pressures; (b) Component Temperatures; (c) Component Volumes

Comment	Gauge Pres. psi.	Gauge Calib. psi.	Atmos. Pres. psi.	Hg Head psi.	Absol. Pres. psia.	Thermocouple 1 mv.	Thermocouple 1 Deg.F	Thermocouple 2 mv.	Thermocouple 2 Deg.F	Thermocouple 3 mv.	Thermocouple 3 Deg.F	Thermocouple M mv.	Thermocouple M Deg.F.	Datum Elev. cm.	Hg. Level cm.	△Elev. cm.	Vol. cc.
H_2S	216	-1.4	13.5	27.0	255.1	1.520	100.0	1.520	100.0	1.528	100.3			79.11	29.22	-49.89	97.9
CH_4	173	-1.2	13.5	16.0	201.3							1.025	78.5	78.73	86.49	+ 7.76	39.1
CO_2	30	-0.2	13.5	15.6	58.9							1.030	78.5	78.65	88.23	+ 9.58	32.3

PART 2: Equilibrium Conditions and Vapor Phase Sampling Data

(a) Equilibrium Pressure; (b) Equilibrium Temperature; (c) Phase Sampling

Gauge Pres. psi.	Gauge Calib. psi.	Atmos. Pres. psi.	Hg Head psi.	Absol. Pres. psia.	Thermocouple 1 mv.	Thermocouple 1 Deg.F	Thermocouple 2 mv.	Thermocouple 2 Deg.F	Thermocouple 3 mv.	Thermocouple 3 Deg.F	Datum Elev. cm.	Hg. Level cm.	△Elev. cm.	Vol. Gas cc.	Atmos. Pres. psi.	Gas temp. Deg.F
1170	+1.0	13.5	15.5	1200	1.521	100.0	1.524	100.2	1.525	100.3	78.96	51.16	-27.80	89.0	13.5	77.4

Quantity of Sample Removed at Cell Conditions:
0.68 cc. by meniscus diff. and 0.66 cc. by pump.
Initial Volume of Vapor Phase = 6.6 cc.

PART 3: Sample Analysis

(a) Tutweiler Analysis

Phase:	Pipette	(1) Initial Iodine cc.	(2) Final Iodine cc.	(3) Iodine Used cc.	(4) Iodine for 100% H_2S	% H_2S
Gas	No. 1	0.3	4.2	3.9	8.3	47.0
	No. 2	0.4	4.1	3.7	7.95	46.6
Liquid	No. 1	0.2	7.2	7.0	8.3	84.3
	No. 2	0.5	7.2	6.7	7.95	84.3

(b) Orsat Analysis

(1) Initial Gas Vol.cc.	(2) Initial +Air cc.	(3) Air Added cc.	(4) After KOH cc.	Vol. CH_4 cc.	% CH_4
51.4	96.4	45.0	67.3	22.3	43.5
52.2	97.0	44.8	50.8	6.0	11.5

APPENDIX II - EXPERIMENTAL PROCEDURE

Each complete test run was separated into several distinct portions which included makeup of the desired system, achievement equilibrium conditions within the system, and finally, the sampling and analysis of the co-existing phases at equilibrium. The operation of the apparatus was a fairly routine matter once a suitable technique had been developed. The only deviation from the routine procedure occurred when systems near the critical composition were being investigated. Under these circumstances, the liquid and vapor compositions were so nearly the same that no samples were removed for analysis, the composition of each phase being assumed to be the same as the total known composition.

1. Preparation of Systems

The temperature of the equilibrium cell was brought up to a desired level before any components were charged. This involved a pre-heating period of several hours. The time required before a run could commence was reduced by switching on the heating system with an automatic timer about four hours in advance. Generally, the vacuum pump was left on between runs to exhaust any remaining gases from the system after the preceding test.

(a) Addition of Hydrogen Sulfide

With the cell temperature at 100 degrees F. the charging commenced by the addition of cylinder hydrogen sulfide to the equilibrium cell. Any air in the line connecting the hydrogen sulfide cylinder and the inlet point of the equipment was first purged by venting the cylinder gas for a few seconds. With reference to the schematic drawing of the

apparatus Fig.5, the venting was accomplished with valves 1, and 4 open, the remainder of the system being isolated by valves 2, 3 and 5.

By closing valve 4 and opening valve 2, the hydrogen sulfide was added directly to the equilibrium cell which had previously been filled with mercury. The mercury was displaced from the cell by the hydrogen sulfide at cylinder pressure into the mercury pump through the connecting line with valves 11, 9, and 14 open. The measuring cells were isolated during this procedure by valve 8. The connecting valve 10 to the Heise pressure gauges was shut during all filling operations to prevent damage to the gauge mechanism from rapid pressure fluctuations. Approximately 100 cc. of gaseous hydrogen sulfide at the cylinder pressure was collected.

After a brief time interval to allow the hydrogen sulfide to reach thermal equilibrium, the volume, temperature and pressure were recorded. The volume was obtained with reference to the calibration curve for the cell Fig.23. This information was used to calculate the quantity of hydrogen sulfide added.

(b) Addition of Methane and Carbon Dioxide

Whereas hydrogen sulfide could be directly added to the equilibrium cell, carbon dioxide and methane had to be determined individually in the measuring cell.

The molar quantities required were fixed by the overall system composition desired and the quantity of hydrogen sulfide already in the equilibrium cell. Hence, the volumes of each component needed in the measuring cell could be predetermined for the pressure at which they

were to be added and at the temperature of the cell. Both the methane and carbon dioxide cylinders were equipped with pressure regulators which permitted collection of the components in the gas phase at any specified pressure below cylinder pressure.

(i) Addition to the Measuring Cell: The order in which methane and carbon dioxide quantities were measured was not fixed, but the procedure was the same for each component.

The equilibrium cell was initially isolated from the system by closing valves 2 and 11. The particular gas cylinder used was connected to the inlet line as was the hydrogen sulfide cylinder, but in this case an additional temporary valve A was included in the connection. Any residual air or hydrogen sulfide in the upper line between the gas cylinder and the vacuum pump was evacuated by the vacuum pump with valves 15, 5, 1 and A open. Valve 6 was also opened to evacuate the measuring cell. When a vacuum was achieved as indicated by the mercury manometer, the measuring cell and the upper line between valves 15 and 5 were completely filled with mercury. The section of line between the gas cylinder and valve 5 was then purged for a brief interval through 4 to the vent line.

The component was then drawn into the measuring cell through the upper line with valves A, 1, 5 and 6 open to the gas flow and 7, 8 and 14 open to the mercury being displaced from the cell. The position of the final mercury meniscus was determined by the use of the cathetometer which had been pre-set to the elevation corresponding to the volume of gas required. When sufficient gas had been collected, valve A was closed to disconnect the gas cylinder. The remaining gas

between A and the measuring cell in the upper line was then forced into the measuring cell by mercury displacement. To accomplish this, valve 7 was first closed, then mercury from the pump was forced through the lower line to the upper by opening valves 9 and 3. With valve 3 open, the mercury could by-pass the equilibrium cell to enter the upper line. All the component was considered to be within the measuring cell when the mercury was observed entering the top of the cell through the sight port.

Valve 6 was then closed together with 3 and 11 and the mercury side of the measuring cell was re-connected to the mercury pump for volumetric adjustments by opening valves 14, 8 and 7. Valves 10 and 12 to the pressure gauges were then opened for the pressure measurements. The volume and temperature measurements were also recorded.

(ii) Addition of Measured Component to Equilibrium Cell

After the phase conditions had been determined, the single component was injected into the equilibrium cell by mercury displacement from the measuring cell. The gas within the measuring cell was first compressed to a pressure greater than that within the equilibrium cell, then valves 6 and 2 were opened to connect the measuring and equilibrium cells. Additional mercury was added to the measuring cell from the pump to fill it and the upper connecting line with mercury. This method forced all the gas into the equilibrium cell through the top connection. Mercury was forced into the upper line until a steady stream was observed running into the equilibrium cell.

The entire procedure was then repeated for the third component.

(c) Achievement of Equilibrium Conditions

After the three components had been added in the desired quantities to the equilibrium cell, the pressure within the cell was increased to the two-phase region being studied. This was accomplished by mercury injection from the pump with valves 14, 9 and 11 open to the circuit.

The remainder of the system was isolated during the equilibrium period with valves 2 and 8 closed. At pressures above 1,000 lb/in.^{2}abs. the connecting valve 12 between the gauges was closed and the 5,000 lb/in.^{2} range gauge was used exclusively.

When the desired pressure was approximately reached, the air bath was disengaged from its lock and rocked vigorously to promote equilibrium between the phases. Generally the system pressure would fall during this process requiring further addition of mercury to the cell. The cell was periodically rocked and additional mercury added until the pressure reading remained constant at the desired level. Usually, an hour was required before the system reached steady state conditions and another hour was allowed to elapse before the sampling operation commenced.

(d) Phase Sampling

The sampling technique permitted the collection of representative phase samples in sufficient quantity to permit the use of volumetric methods in the quantitative analysis of the components.

(i) Sample Collector: The samples were collected at atmospheric conditions in a water jacketed pyrex tube of approximately 100 cc. internal capacity. The sample collector is shown by Fig.2. Samples

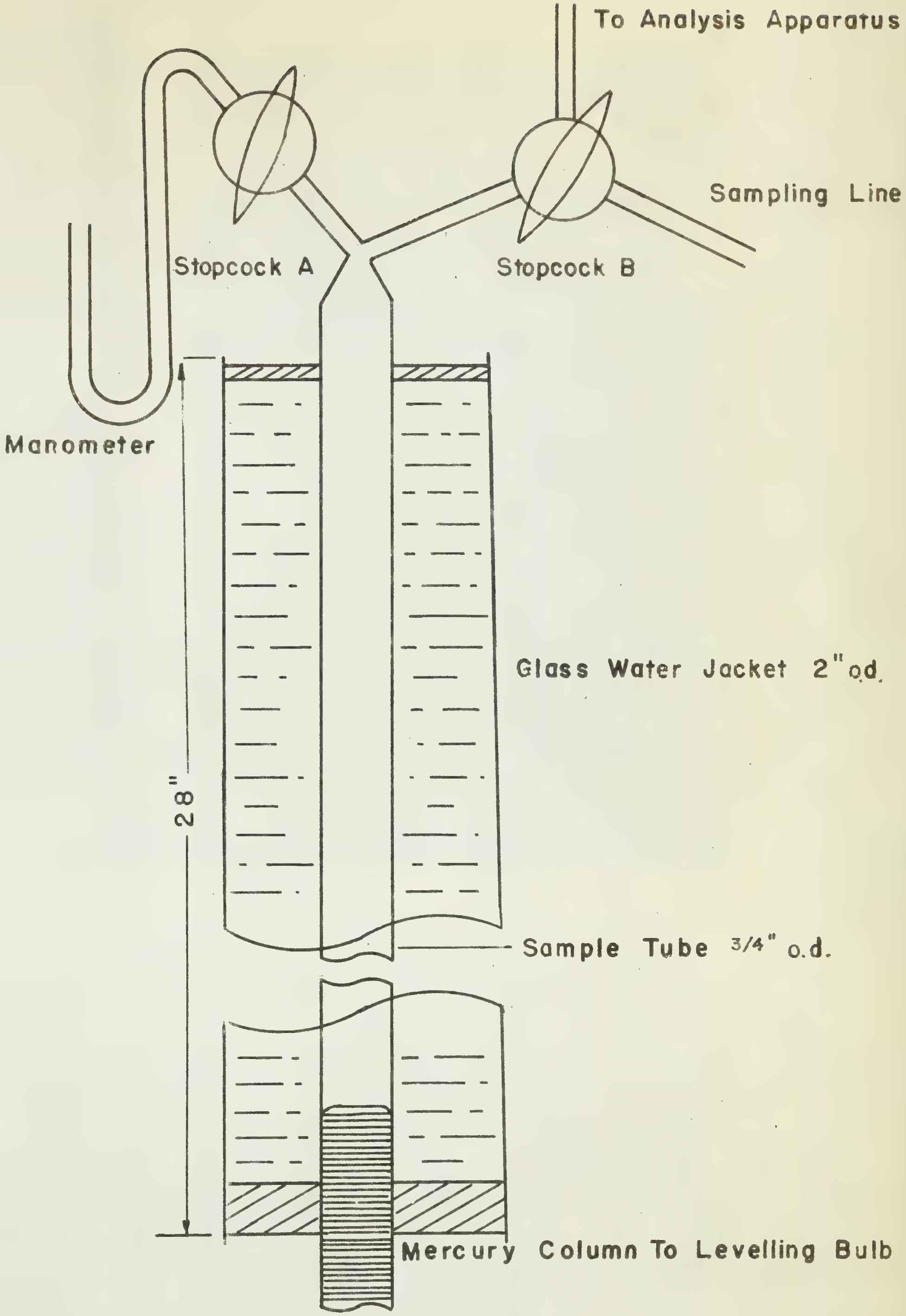

FIG. 21 SAMPLE COLLECTOR

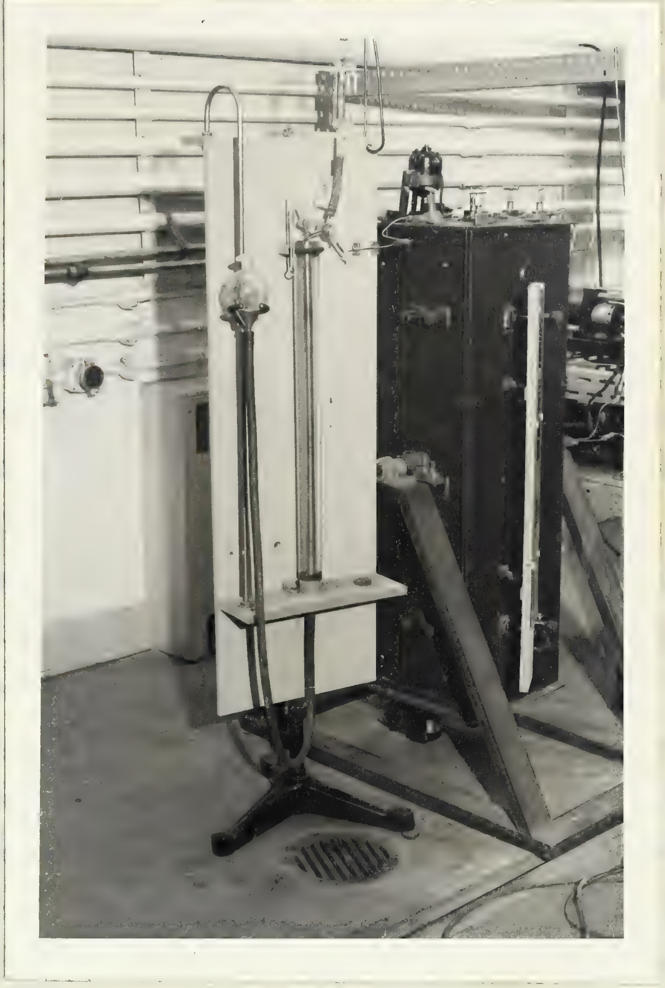

Plate 5: Sample Collector and Air Bath

were obtained by the displacement of mercury from the tube into a glass levelling bulb connected with a rubber hose to the bottom of the glass tube. The level of the mercury in the tube could be adjusted by moving the levelling bulb up or down beside the tube.

The top of the sample tube was joined by means of a Y connector to two pyrex stopcocks marked A and B. Stopcock A connected the tube to a small glass U-tube filled with mercury which was used as a manometer for comparison of pressure within the tube to atmospheric pressure. The two-way stopcock B joined the sample tube either to the sampling point of the equilibrium cell, or to the analysis equipment. A short length of Ruska tubing bonded to the glass tubing at the stopcock with Armstrong Cement constituted the glass to metal joint on the sampling line. Plate 5 shows the sampler and its mounting stand in conjunction with the equilibrium cell.

(ii) Sampling Procedure for Gas Phase: When equilibrium was obtained in the system the air bath was firmly clamped in a vertical position and connected to the sample collector at the sample line. The cell was isolated from the pump by closing valve 9 and mercury was pushed into the partially empty gas collector through the upper mercury line. The mercury passed through the measuring cell and upper line from the pump. This expelled all air from the connection between cell and sampler into the sampler. The sampling tube was then completely filled with mercury from the levelling bulb. Stopcock A was left closed during this operation. Valve 8 was then closed and the pump to cell circuit re-opened through valve 11.

The initial gas sample could then be taken. The procedure required two operators for successful completion. The first operator slightly

cracked valve 2 which permitted a slow flow of gas to enter the sampler through valve 1 and stopcock B and the gas expanded to atmospheric pressure. The second operator closely watched the pressure gauges and at the first indication of a pressure drop commenced injecting mercury into the cell to replace the volume of gas being removed. The mercury was added at a rate just sufficient to maintain the system pressure constant. Approximately 80 cc. of sample at atmospheric conditions would be collected in two minutes expanding from 1.5 cc. to 0.5 cc. of gas at the cell conditions.

When most of the mercury in the collector had been displaced into the levelling bulb by the entering gas, sampling was stopped by shutting valve 2. The residual gas in the collector to cell line was then displaced by mercury from the pump into the collector.

Stopcock B was closed and the pressure of the sample was brought to atmospheric by use of the levelling bulb and manometer. The volume of sample at atmospheric conditions was obtained using the cathetometer to determine the mercury level and then referring to a volumetric calibration curve for the sample tube. The temperature of the gas was assumed to be the same as the water in the surrounding water-jacket.

The volume of the sample removed at cell conditions was obtained by consideration of the elevation changes in the mercury miniscus during the sampling. This elevation change gave the quantity of mercury injected during the sampling, which was also equivalent to the volume of sample removed, providing the system pressure was the same after sampling as before. A check on the quantity of mercury added was obtained from the difference in the elevations in the liquid phase meniscus before and after the sampling. The difference in the mercury meniscus elevations and that for the liquid phase should have been the

same if the elevations were correctly recorded. As the quantity of sample removed at cell conditions was very small, the equivalent amount of mercury added had to be determined fairly accurately or large errors would arise in the calculation of the liquid composition. (See Sample Calculation Appendix III). Another independent check of the mercury added was obtained by use of the volumetrically calibrated mercury pump.

Two gas samples were usually taken to determine the composition of the vapor phase. The machined fitting between the Ruska Valve 2 and the equilibrium cell was purposely limited to a small volume to reduce dead space above the equilibrium cell proper. However, a portion of the final component would apparently be trapped here without reaching true equilibrium with the remainder of the system. Since the initial sample served to purge this volume, it frequently analyzed too high in the final component which had been added. The second sample was therefore used for calculating the equilibrium composition.

(iii) Liquid Phase Sample: The liquid phase was removed from the cell after the vapor phase had been completely removed, and vaporized in the sample collector. This was accomplished by slowly displacing it with mercury to keep the system at constant pressure. The gas was vented off through valve 4 to the atmosphere. The quantity of liquid sample removed was not required for purposes of calculation.

(e) Analytical Procedure

The gas mixtures were analyzed by Orsat for methane and by the Tutweiler titration method for hydrogen sulfide. Carbon dioxide was determined by difference as no independent analysis was available for it.

The gas mixture in the Orsat determination was passed into a bubbler containing saturated potassium hydroxide solution which removed both hydrogen sulfide and carbon dioxide leaving methane. The initial sample was diluted with a known volume of moisture-free air prior to passing it through the bubbler. Had air not been added many of the samples low in methane would yield an insufficiently measurable volume after the carbon dioxide and hydrogen sulfide removal. The analysis was on a water-free basis since the only source of moisture was from the potassium hydroxide solution. However, the partial pressure of water above saturated potassium hydroxide solutions at room temperature is only 1.5 mm. so no volumetric error was introduced from this source. The methane analysis had good reproducibility, since duplicate samples of the same system agreed to 0.2%.

The hydrogen sulfide samples were taken from the gas collector in two 5 cc. pipettes formed by the fusion of two 5 mm. pyrex straight stopcocks to a larger pyrex center section. Plate 6 shows a view of a pipette together with the Tutweiler Apparatus. Pipette samples were secured at atmospheric pressure, the pipettes having been previously evacuated. The hydrogen sulfide was titrated with 0.05 N iodine in the 500 cc. Tutweiler burette with a starch solution indicator. The quantity of hydrogen sulfide in the sample was obtained from the ratio of the actual iodine required to that required for the same volume of pure hydrogen sulfide. Corrections were usually necessary to allow for the daily variation in atmospheric pressure since the quantity of sample in the pipette was proportional to the atmospheric pressure.

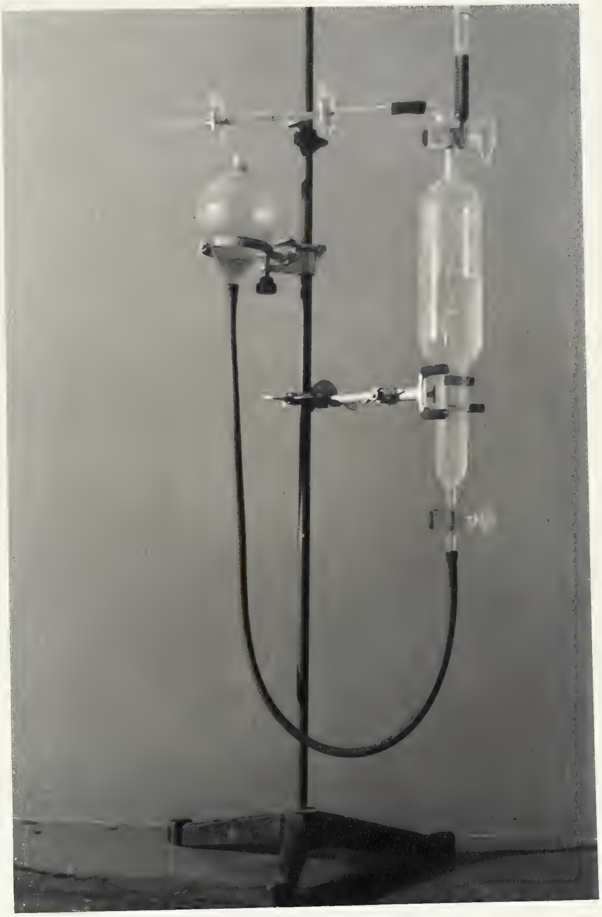

Plate 6: Tutweiler Appratus and Sample Pipette

To minimize the errors in the Tutweiler determination, duplicate portions of the same sample were tested and the average values are reported. These duplicate samples usually agreed within 0.5%.

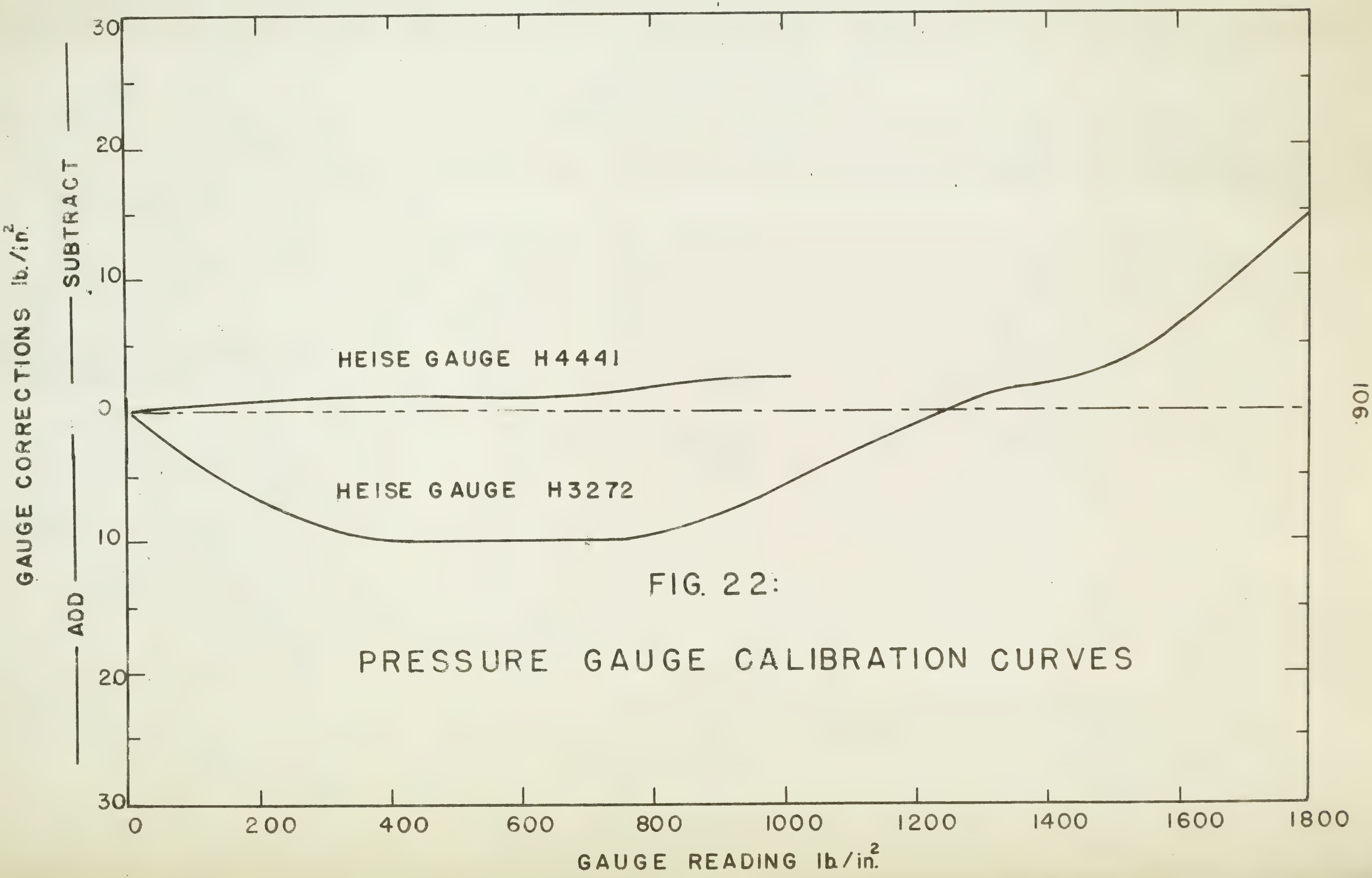

FIG. 22:

PRESSURE GAUGE CALIBRATION CURVES

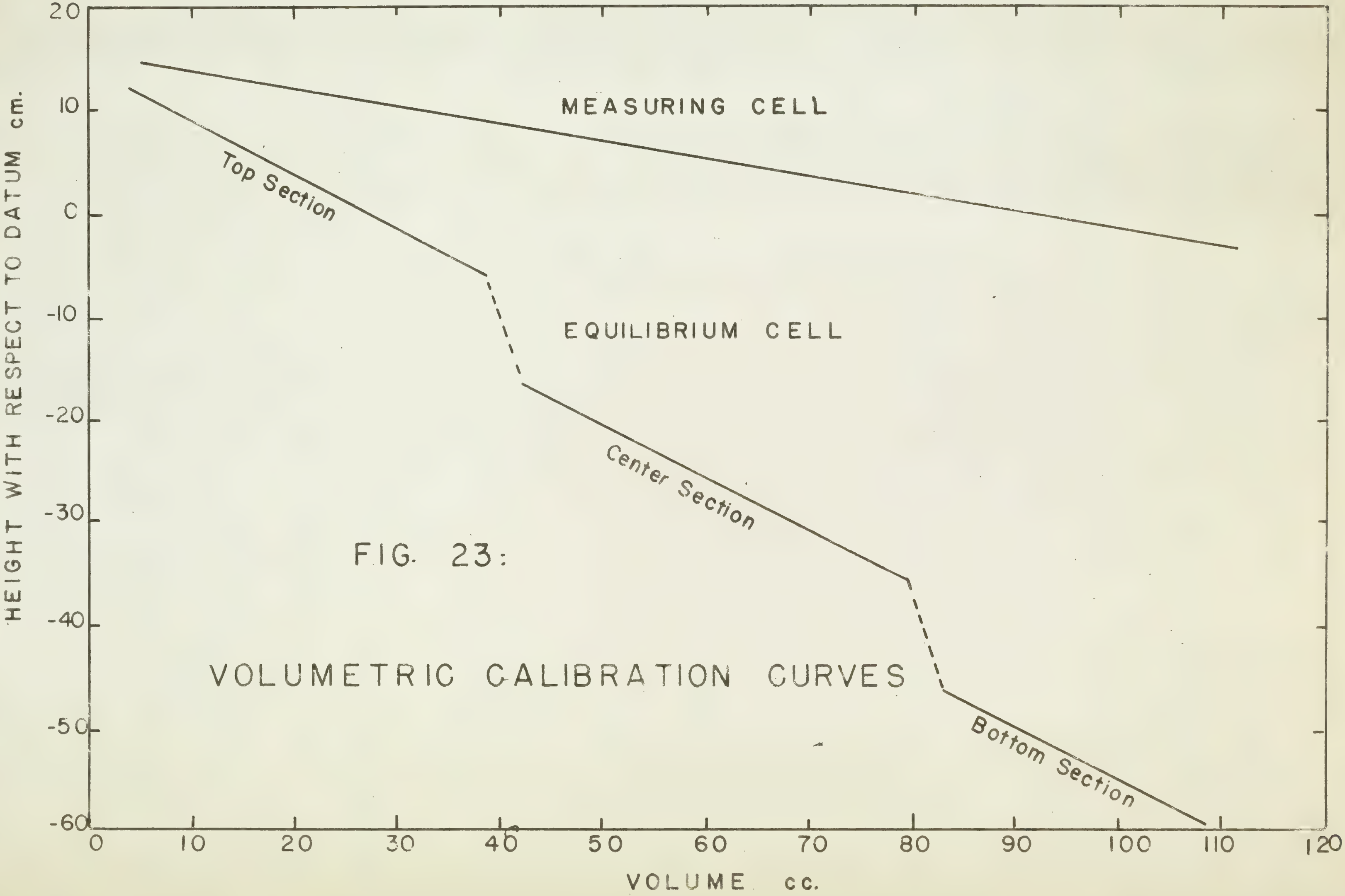

FIG. 23:

VOLUMETRIC CALIBRATION CURVES

APPENDIX III

Results and Calculations for Run No. II - II at $P = 1200\ \mathrm{lb/in.^2 abs.}$

$T = 100$ Degrees F.

(Data recorded during the run are listed in Table 11 Appendix I)

1. Quantity of Components Added to Equilibrium Cell

(a) Quantity of H_2S Added:

Phase Conditions: (a) $P = 255\ \mathrm{lb/in.^2 abs.}$

(b) $T = 100$ Deg. F.=560 Deg. R.

(c) $V = 97.9$ cc.

(d) $Z = 0.867$

(e) $R = 670 \dfrac{\mathrm{lb.\ cc.}}{\mathrm{in.^2(^oR)g.mole}}$

$$\text{Since } n = \frac{PV}{ZRT}$$

$$\text{Then } n = \frac{255(97.9)}{0.867(670)560}$$

$$n = \underline{0.0766} \text{ g.moles}$$

(b) Addition of CH_4

(i) Calculation of CH_4 Volume Required:

The desired total composition in the heterogeneous region at $1200\ \mathrm{lb/in.^2 ab.}$ was:

$$H_2S = 0.75 \text{ mole fraction}$$

$$CH_4 = 0.20$$

$$CO_2 = \underline{0.05}$$

$$1.00$$

The moles of CH_4 required (n) were roughly determined from the ratio:

$$\frac{n}{n+0.0766} = 0.20$$

$$n = 0.0191 \text{ g.moles}$$

CH_4 was added to the measuring cell at 200 lb/in.^{2}abs. at a cell temperature of 79 Deg. F. The compressibility factor for CH_4 was 0.976 at these conditions.

$$\text{Since } V = \frac{nZRT}{P}$$

$$\text{Then } V = \frac{.0191(0.976)670(539)}{200}$$

$$V = \underline{34}\text{ cc.}$$

Therefore for 0.0191 **g.moles** of CH_4 at 200 lb/in.^{2}abs. at 79 Deg. F., the total volume of 34.0 cc. are required.

(ii) Actual Quantity of CH_4 Added:

Phase Conditions: (a) P = 201.3 lb/in.^{2}abs.
(b) T = 78.5 Deg. F.
(c) V = 39.4 cc.
(d) Z = 0.976

$$n = \frac{201.3(394)}{0.976(670)538.5}$$

$$n = \underline{0.0225}\text{ g. moles}$$

(c) The quantity and volume of CO_2 required fora mole fraction of 0.05 in the system was determined in the same manner as for the CH_4 addition. A total of 0.00541 moles of CO_2 were added at phase conditions of 78.5 Deg. F., 58.9 lb/in.^{2}abs. and 32.3 cc. The compressibility factor for CO_2 at these conditions was 0.975.

(d) The total system contained:

	Moles	Mole Fraction
H_2S	0.0766	0.732
CH_4	0.0225	0.216
CO_2	0.00541	0.052
	0.10451	1.000

2. Analysis of Phases at Equilibrium:

	Gas Phase	Liquid Phase
H_2S	0.47	0.843
CH_4	0.435	0.115
CO_2	0.095	0.042
	1.000	1.000

3. Calculation of Liquid Analysis:

The liquid composition was calculated by a material balance on the system. The moles of vapor phase sample removed from the equilibrium cell were obtained from the volume, pressure, and temperature of the sample in the sample collector. A compressibility factor of unity was assumed in the calculation since the sample pressure was atmospheric. The volume of the vapor phase at the cell conditions removed during the sampling was also determined. The initial quantity of the vapor phase prior to sampling, was then determined, using a total observed volume of the vapor phase in the cell. Since the analysis was known as well as the total quantities of each component originally in the cell, the component quantities in the liquid phase could be determined.

For Run No. II - II:

The quantity of vapor phase sample in the collector was: 89.0 cc. at 77.4 Deg.F., and 13.5 lb/in.^{2}abs.

Therefore, the moles of sample removed $= \dfrac{89.0(13.5)}{670(537.4)}$

$= \underline{3.34\text{x}10^{-3}}$ g.moles

The initial volume of the vapor phase at cell conditions was 6.6 cc. and the volume of the phase removed during the sampling was 0.68 cc.

Therefore, the total quantity of vapor phase prior to sampling was:

$$\frac{6.6(3.34\times10^{-3})}{0.68} = \underline{0.0324} \text{ g.moles.}$$

Then the remaining H_2S in the liquid phase:is:

$$= 0.0766 - 0.47(.0324) = \underline{0.06138} \text{ g.moles}$$

The remaining CH_4 = 0.0225 - 0.435(0.0324) = 0.0084 g.moles

The remaining CO_2 = 0.00541 - 0.095(0.0324) = 0.00233 g.moles

Then mole fraction H_2S in the liquid phase = 0.85

CH_4 " " " = 0.116

CO_2 " " " = $\underline{0.032}$

0.998

4. Calculation of Compressibility Factor Z_m for the Vapor Phase at Equilibrium Conditions

Phase Variables for the Vapor Phase at Equilibrium Conditions:

$V = 6.6$ cc.^{3}

$P = 1200$ lb/in.^{2}abs.

$T = 560^\circ$R.

$n = 0.0324$ g.moles (Part 3)

Then:

$$Z_m = \frac{1200(6.6)}{0.0324(670)560} = \underline{0.65}$$

5. Calculation of Equilibrium Constants

(i) Experimental Equilibrium Constants

From equation (13):

$$K_{CO_2} = \frac{0.095}{0.042} = 2.26$$

From equation (14):

$$K_{H_2S} = \frac{0.47}{0.843} = 0.558$$

From equation(15):

$$K_{CH_4} = \frac{0.435}{0.115} = 3.78$$

(ii) Theoretical Equilibrium Constants

From equation (11), the theoretical equilibrium constant is the ratio of the vapor pressure to the total pressure.

At 100 Deg.F. the vapor pressure of H_2S is 410 lb/in.^{2}abs.

The extrapolated vapor pressure of CO_2 is 1220 lb/in.^{2}abs.

The extrapolated vapor pressure of CH_4 is 4200 lb/in.^{2}abs.

Then at 1200 lb/in.^{2}abs.:

$$\text{Theoretical } K_{CO_2} = \frac{1220}{1200} = 1.02$$

$$\text{Theoretical } K_{H_2S} = \frac{410}{1200} = 0.342$$

$$\text{Theoretical } K_{CH_4} = \frac{4200}{1200} = 3.50$$

6. Calculation of Activity Coefficients:

From equation (12) the activity coefficient is the ratio of the actual equilibrium constant to the theoretical.

$$\text{Activity coefficient for } CO_2 = \frac{2.26}{1.02} = 2.22$$

$$\text{Activity coefficient for } H_2S = \frac{0.558}{0.342} = 1.63$$

$$\text{Activity coefficient for } CH_4 = \frac{3.78}{3.50} = 1.08$$

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